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Ion Pair Dissociation Effects of Aza-based Anion Receptors on Lithium Salts in Polymer Electrolytes

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ABSTRACT

The addition of aza-based anion receptors greatly increases the conductivity of polymer electrolytes based on LiCl or KI complexes with poly(ethylene oxide) (PEO). In some cases the conductivity increase is more than two orders of magnitude. Also the addition of the anion acceptors imparts a rubber like consistency to the normally stiff PEO salt films. Ion-ion, ion-polymer and anion-complex interactions were studied using Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy at the K and Cl K edges and at the I L_I edge. The NEXAFS results show that Cl^- and I^- anions are complexed with the nitrogen groups of the anion receptors. The degree of complexation is related the chain length of the complexing agent and the number of $R=CF_3SO_2$ groups that are used to substitute for the amine hydrogen atoms in these aza-ether compounds. NEXAFS spectra at potassium K edge provide supplemental evidence for the ion pair dissociation effects of the anion receptors. The results show that dissociated K^+ cations are complexed with oxygen atoms of the PEO chains.

INTRODUCTION

We have synthesized a new family of aza-ether based compounds which are anion receptor molecules. When these compounds are added to non-aqueous liquid electrolytes using lithium salts, the ionic conductivity is dramatically increased. Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra obtained for THF solutions of LiCl and LiI, containing aza- compounds, show that the Cl^- and I^- anions are complexed by the anion receptors [1]. In this paper, we report on conductivity enhancement by these anion receptors when used as additives in PEO based polymer electrolytes. NEXAFS spectroscopy, at the Cl and K K edges and at the I L_I edge, was used to probe ion-ion, ion-polymer and anion complex interactions in these electrolytes.

EXPERIMENTAL

The structures and nomenclature of the new family of aza-based anion receptors, used in this study, are given in Fig. 1. For the conductivity study electrolyte films were prepared as follows. Solutions of 0.2M LiCl in acetonitrile and 0.2M LiCl + 0.2M L6R in acetonitrile were mixed with 2 wt% PEO (Aldrich MW=$5x10^6$) in acetonitrile with 1:16 of salt:oxygen ratio. Sample films were cast on a nickel foil and dried in vacuum oven at 50 °C for 12 hours. After that, FTIR spectra were taken to insure that no acetonitrile residue remained in the sample. The films used in the NEXAFS study at Cl^+ edge were prepared in the same way. The solutions containing 0.2M KI + 0.2M of the anion complexing agent (L2R, L4R, L5R or L6R) in acetonitrile were mixed with acetonitrile solution of PEO (2 wt%). The solutions were used to prepare thin film samples which were cast on Kapton films and dried at 50 °C for 20 minutes before NEXAFS measurements. The salt:oxygen ratio in these films was 1:4.

Conductivity measurements were carried out using a Hewlett-Packard 4129A Impedance Analyzer in the frequency range from 5Hz to 10 MHz.

NEXAFS measurements were made at Beam Line X19A of the National Synchrotron Light Source. The data were collected as fluorescence excitation spectra using a large solid angle ionization chamber as the fluorescence detector. As the incident x-ray energy was scanned through a certain energy edge, the ejected photoelectrons sequentially probe empty electronic levels of the sample being studied, resulting in fine structure in the near edge absorption spectrum. The relaxations of these excited states take place by either the emission of Auger electrons or fluorescence photons. The features of the spectrum depend on bonding, valence, and coordination symmetry of the absorbing ions such as Cl^-, I^-, or K^+ in the sample. By comparing the spectra with reference compounds, the degree of complexation can be studied through the changes in the spectra due to the changes of the coordination of the absorbing ions.

RESULTS AND DISCUSSION

The ionic conductivity at 25 °C, 35 °C, 45 °C, 55 °C, and 65 °C for PEO_{16}(LiCl) and PEO_{16}(LiCl + L6R) are listed in Table I. An Arrhenius plot of the same data is shown in Fig. 2. At each temperature, the ionic conductivity of the sample containing anion receptor L6R and LiCl salt (sample B) is two orders of magnitude higher than the conductivity of sample A which contains the LiCl salt only. The $(PEO)_{16}$LiCl electrolyte was a stiff film, whereas the films containing the anion complexing agents were rubber like. This is due to a plasticizing effect caused by the L6R additive similar to that caused by the imide salt $LiN(SO_2CF_3)_2$ which suppresses crystallinity of PEO-salt complexes [2].

The NEXAFS spectra at chlorine K edge, plotted in Fig. 3, are for PEO based electrolyte samples as indicated in the plot, where L2R, L5R, and L6R represent the linear aza-compounds with either 2, 5, or 6 R=CF_3SO_2 groups with structures as shown in Fig. 1. The salt:oxygen ratio was 1:16. Curve (a) and (d) are spectra for the same samples used in conductivity studies. The "white line" peak, between 2820 and 2840 eV, is due to dipole-allowed transitions to final states of *p* symmetry. The structure of the "white line" is very

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sensitive to the coordination of the absorbing atom. It has been used to study the coordination of K in a KI-(PEO) complex [3]. The white line in curve (a) for $PEO_{16}(LiCl)$ is a broad peak. The same structures is found for Cl^- in free ion state, such as LiCl and KCl in dilute aqueous solutions. With the symmetric coordination of the hydrated ion the $3p$ final states of the Cl^- are close to being degenerate and the transition feature is a broad peak. White line peak splitting can occur if there is an asymmetric distribution of atoms (or molecules) surrounding the Cl^- with strong bonding. The more asymmetric the distribution is, the stronger the splitting effect will be. The asymmetric local field experienced by each of the degenerate $3p$ final states of Cl^- is different and the degeneracy is lifted. This results in a splitting of the absorption peak. In the crystal state, however, the strong ionic bounding between the Li^+ and Cl^- does not cause any white line splitting, because of the high degree of symmetry in the rock salt structure and the weak scattering factor of Li^+. In curve (b), the "white line" did not change significantly when the L2R was added into the system indicating that L2R does not form a strong enough complex with Cl^- to create a noticeable structural change in the NEXAFS spectrum. We classify these anions in curve (a) and (b) as uncomplexed anions. In curve (c) and (d), a clear split was observed when R-substituted aza-ether compound L5R and L6R were added into the electrolyte. Feature (A) becomes a strong sharp peak. This presents strong evidence that Cl^- is indeed complexed with nitrogen atoms of the aza-based anion receptors.

The NEXAFS spectra at iodine L_I edge, plotted in figure 4, are for PEO based electrolyte samples: (a) PEO_4(KI + L2R), (b) PEO_4(KI + L4R), (c) PEO_4(KI + L5R), and (d) PEO_4(KI + L6R). The spectrum for PEO_4(KI) was similar to that for PEO_4(KI + L2R) and is omitted. In the same fashion as in Fig. 3 for chlorine edge, feature (A) served as an indicator of the degree of complexation between the I^- ions and the aza compounds [1]. The relationship between the relative intensity of feature (A) and the chain length of aza compounds is clear. Feature (A) is not observed in curve (a), when L2R with only two R groups was used as additive. In curve (b) for sample containing L4R which has four R groups, feature (A) appears as a small shoulder. In curve (c) and (d) for samples containing L5R and L6R, feature (A) becomes a clear peak. It can be concluded that the degree of complexation increases with increasing chain length and the number of R groups of the anion receptors. These results are identical to those in liquid non-aqueous electrolytes containing lithium halide salts and aza compounds as reported in our early studies [1].

Having studied the ion pair dissociation effects of these new anion receptors on LiCl and KI through chlorine and iodine edges, we are interested in knowing what we can learn from the cation edge studies. However, the edge energy of lithium is too low for NEXAFS study. Therefore, KI salt was used and potassium *K* edge NEXAFS spectra were studied. The sample set that was used for the iodine L_I studies was also used for the potassium K edge studies. Figure 5 show potassium K edge spectra for a set of reference compounds. These are KI salt, PEO_4(KI), PEO_8(KI), and a 0.5M aqueous KI solution. The respective spectra are plotted in Fig. 5 as curves (a), (b), (c), and (d). In curve (a), the white line is split into three features (A), (B), and (C), due to the strong ion interaction between the K^+ and I^- in crystalline state. In curve (b), for the sample of PEO_4(KI), the relative intensity of feature (C) is increased in the expense of reduced intensity of feature (A). However, all (A), (B), and (C) are still clear peaks. The white line splitting in Fig. 5 can be attributed to two sources, namely undissolved crystalline KI, KI ion pairs and higher aggregates of KI

in PEO. This will be further studied by x-ray diffraction. In curve (c) for the sample of $PEO_8(KI)$, feature (A) becomes a shoulder, feature (B) and (C) are merged into a broad peak. In curve (d) for 0.5M KI salt in aqueous solution, the relative intensity of feature (A) is further reduced. The decrease of the relative intensity of feature (A) and the broadening of feature (B) and (C) in curve (c) for the sample with lower salt: oxygen ratio are due to the complexation between the K^+ and the oxygen atoms of the PEO chain. This shows how ion dissociation changes the potassium K edge structure [3]. The spectra in Fig. 5 were used as references to study the effect of the anion acceptors and ion dissociation on the environment around the potassium ions.

Fig. 6 shows the effect of the addition of various anion complexing agents on the potassium K edge NEXAFS spectra. Data are shown for: (a) PEO_4(KI + L2R), (b) PEO_4(KI + L4R), (c) PEO_4(KI + L5R), and (d) PEO_4(KI + L6R). A comparison this data with the data in Fig. 4 shows how the addition of the anion complexing agents also changes the environment around the cation. In Fig. 6 curve (a) and curve (b) are almost the same as curve (b) in Fig. 5 for $PEO_4(KI)$, indicating the existing of undissolved KI and strong ion pairing. In curve (c), feature (B) and (C) merged into a broad peak indicating the complete dissolution of the KI salt and the dissociation of K^+ cation from the I^- caused by L5R. In curve (d), the intensity of feature (A) is further reduced indicating a stronger ion pair dissociation effect caused by L6R. This is a clear evidence the addition of L5R and L6R to the polymer electrolyte with high salt concentration, promotes salt dissolution and ion dissociation. The dissociated K^+ cations form complexes with the oxygen atoms of the PEO chain. The effects of the chain length of the anion receptors on the potassium NEXAFS, seen in Fig. 6, follow the same trend as the NEXAFS for the iodine, seen in Fig. 4. This provides complementary confirmation of the formation of anion complexes and the promotion of salt dissolution and ion dissociation on the addition of aza complexing agents with longer chain length.

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Table I. Ionic Conductivity of $PEO_{16}(LiCl)$ and $PEO_{16}(LiCl + L6R)$ at Various Temperatures

Temperature	Conductivity (S cm^{-1}) Sample A $PEO_{16}(LiCl)$	Conductivity (S cm^{-1}) Sample B $PEO_{16}(LiCl+L6R)$
25 °C	1.0×10^{-8}	4.7×10^{-6}
35 °C	8.4×10^{-8}	1.2×10^{-5}
45 °C	2.0×10^{-7}	3.0×10^{-5}
55 °C	1.4×10^{-6}	6.0×10^{-5}
65 °C	2.8×10^{-6}	1.2×10^{-4}

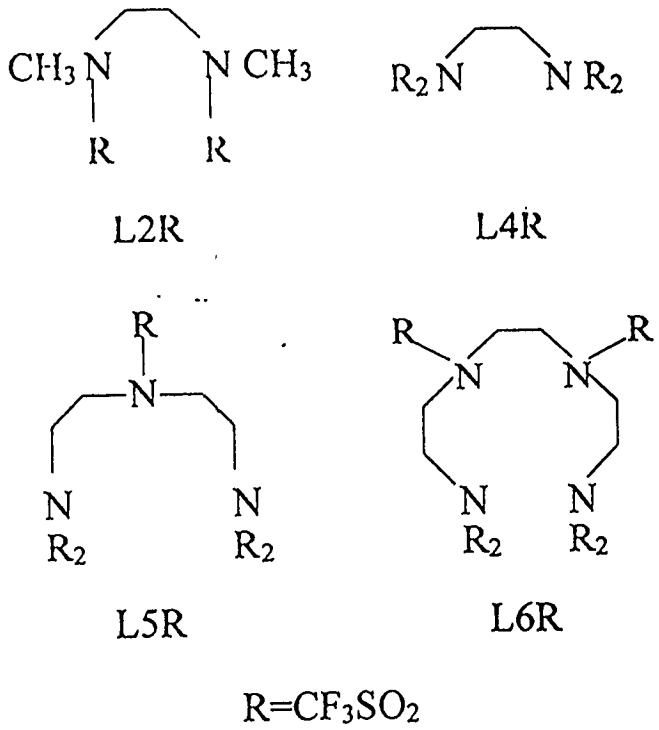

Figure 1. Chemical structure of aza-ether anion receptors

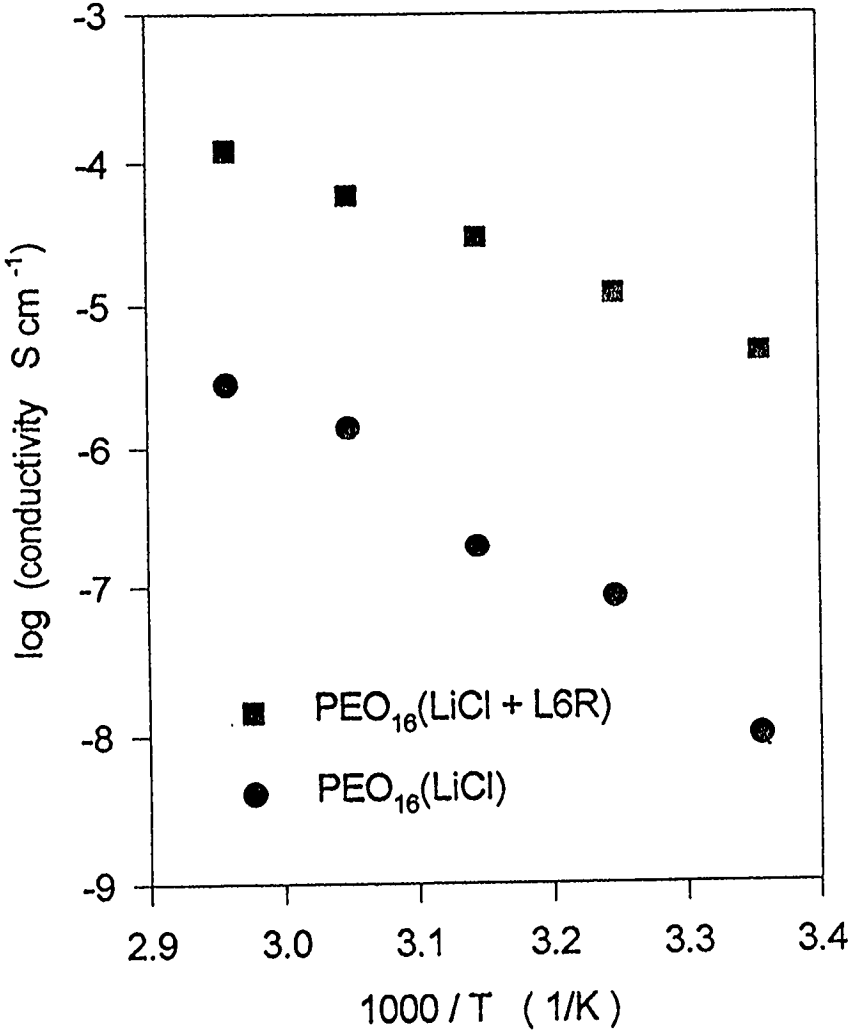

Figure 2. Ionic conductivity versus inverse temperature for $PEO_{16}(LiCl)$ and $PEO_{16}(LiCl + L6R)$

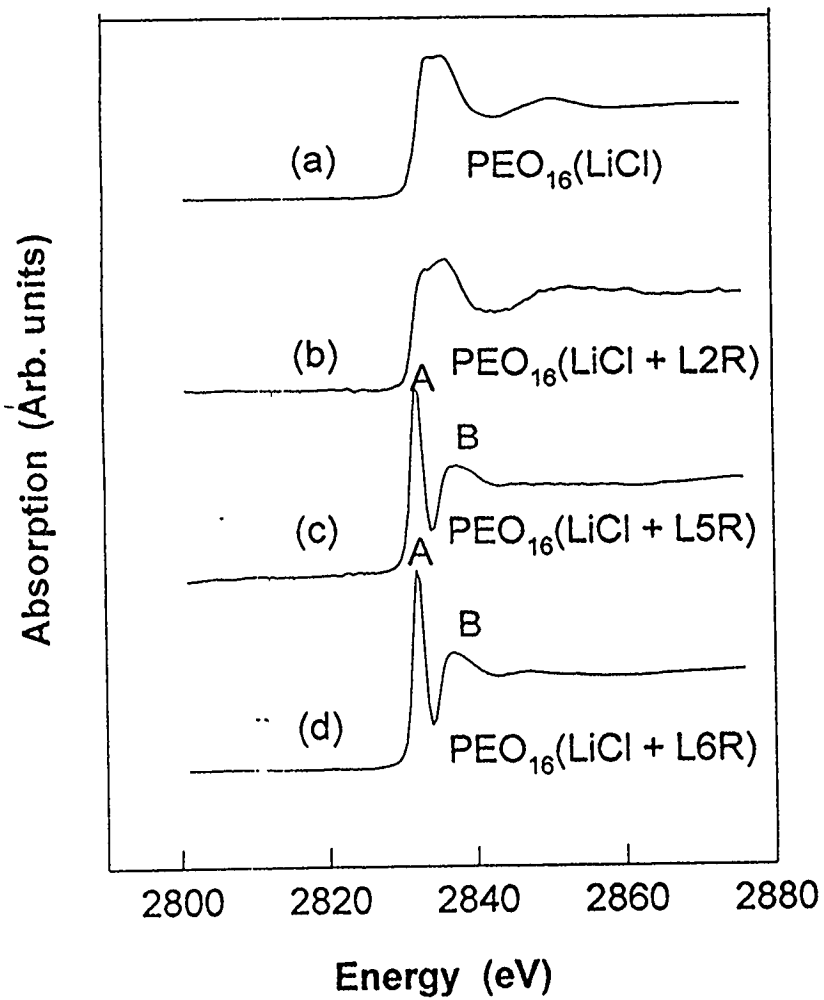

Figure 3. NEXAFS spectra at chlorine *K* edge for: (a) $PEO_{16}(LiCl)$, (b) $PEO_{16}(LiCl + L2R)$ (c) $PEO_{16}(LiCl + L5R)$, and (d) $PEO_{16}(LiCl + L6R)$

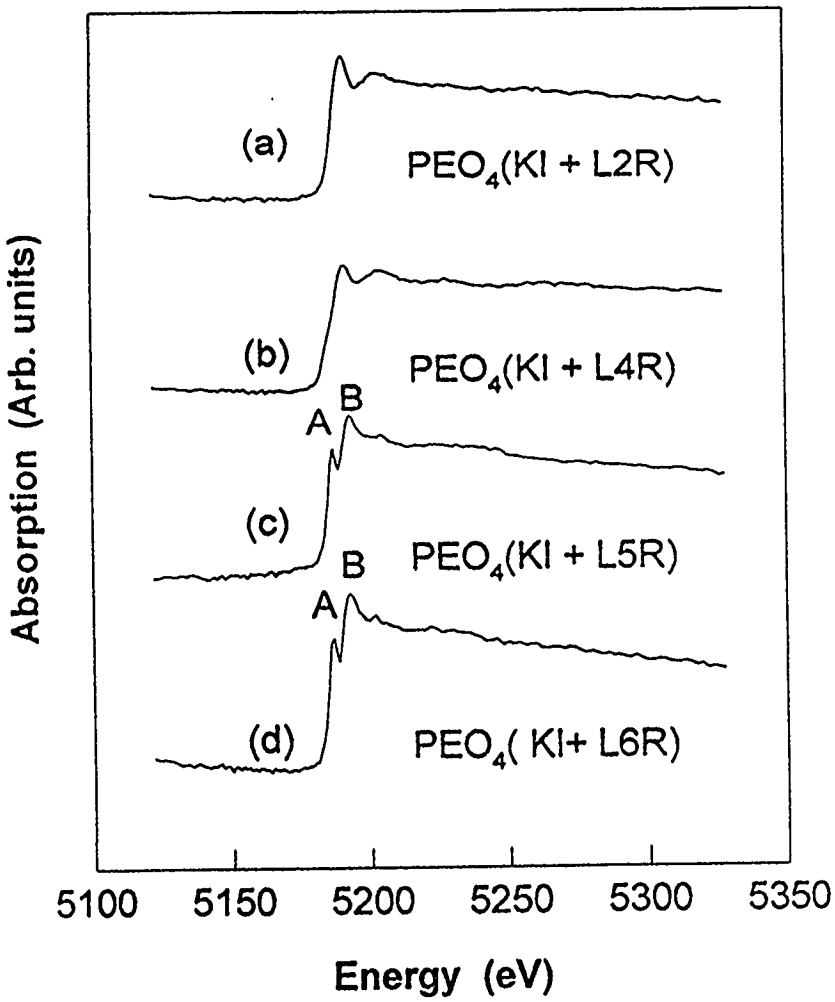

Figure 4. NEXAFS spectra at iodine L_I edge for: (a) $PEO_4(KI + L2R)$, (b) $PEO_4(KI + L4R)$ (c) $PEO_4(KI + L5R)$, and (d) $PEO_4(KI + L6R)$

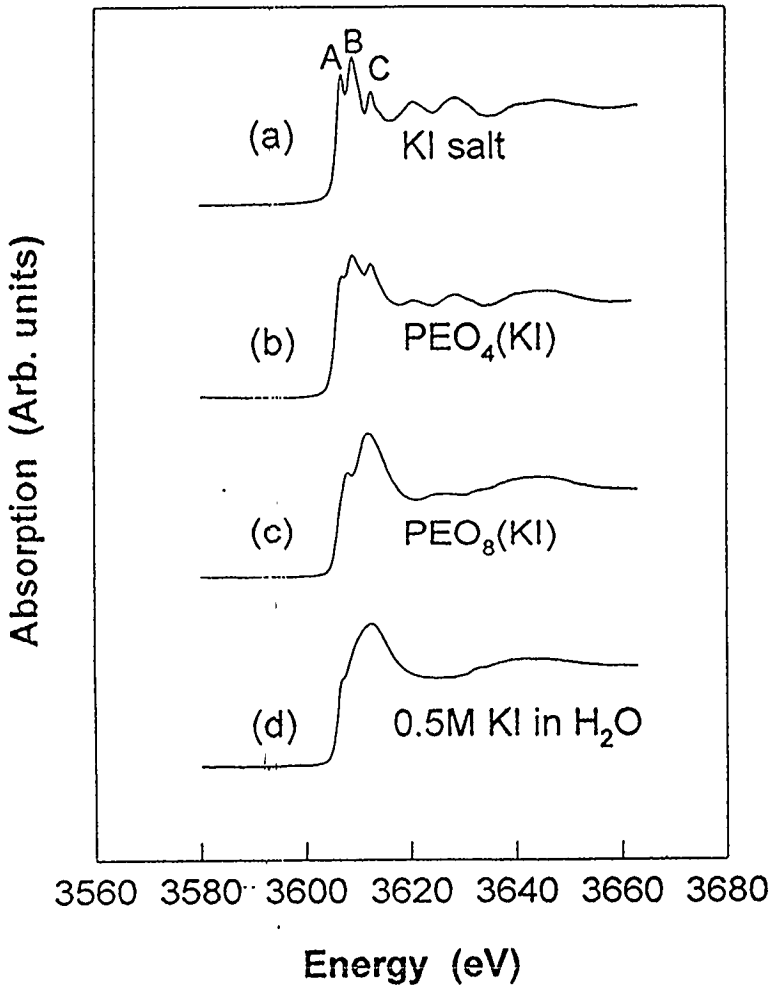

Figure 5. NEXAFS spectra at potassium *K* edge for: (a) KI salt, (b) $PEO_4(KI)$ (c) $PEO_8(KI)$, and (d) 0.5M KI in H_2O

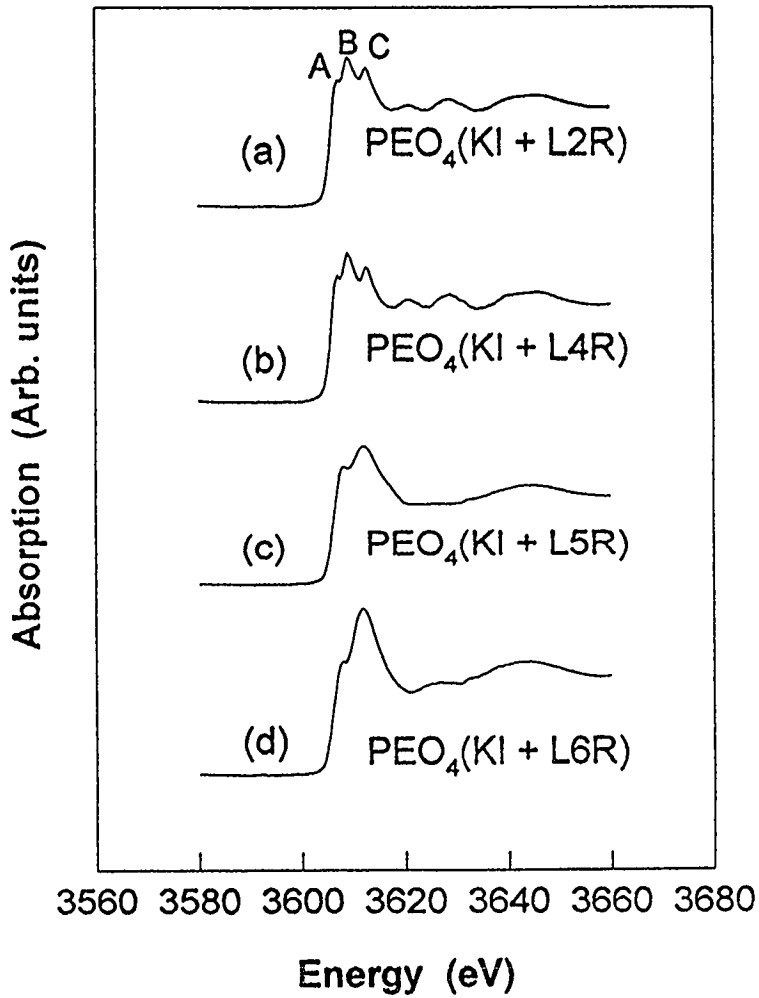

Figure 6. NEXAFS spectra at potassium *K* edge for: (a) $PEO_4(KI + L2R)$, (b) $PEO_4(KI + L4R)$ (c) $PEO_4(KI + L6R)$, and (d) $PEO_4(KI + L6R)$