

Solid state intercalation of barium into poly(para-phenylene): TEM, EELS and ESR characterizations

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Abstract

Compressing together divided barium and poly(para-phenylene) results in the intercalation of the metal into the polymer. Electron energy loss spectroscopy (EELS) analysis indicates that an intercalation level of 0.24 barium ions per phenyl unit can be achieved and that the oxidation state of the intercalated barium is rather +2 (Ba^{2+}). Both transmission electron microscopy and electron spin resonance studies show that the distribution of the intercalant in the polymer is very inhomogeneous.

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1. Introduction

Conjugated organic polymers can react with electron donating or accepting species to give, in the intercalated state, compounds exhibiting a high electrical conductivity. Poly(para-phenylene) (PPP) or $(\text{C}_6\text{H}_4)_x$ is one of the most-studied conductive polymer. The intercalation of various species, such as alkaline ions (Li^+ , Na^+ , K^+ , etc.), can be achieved either by chemical or electrochemical techniques [1–4]. AsF_6^- , I_3^- , and BF_4^- are also good p-type dopant ions for PPP [5,6]. Only few works reported on the intercalation of divalent ions for PPP; Kaner and coworkers [7–9] studied the reaction of PPP and polyacetylene with strong reducing solutions containing divalent cations (Ca^{2+} , Sr^{2+} , Ba^{2+} , etc.) and prepared by dissolving alkaline earth metals in liquid ammonia. With this chemical technique, the solvent molecules are usually cointercalated with the metal ions. It was assumed that these solvent molecules could participate in the charge transfer between the polymer chains and the dopant ions. The resulting electrical and magnetic properties of such ternary compounds can be different from those of the parent binary compounds, which do not contain co-inserted solvent molecules. In order to avoid this solvation effect, we investigated the direct intercalation of barium ions into PPP using the chemical method of the compression of powder. Stoichiometric

quantities of PPP and Ba powders were mixed and pressed, resulting in the direct reaction of the metal with the polymer, which was consequently reduced. The negative charges of reduced PPP are then compensated by the positive charge of barium ions that intercalate into the structure of the polymer. The Ba/PPP compounds were characterized by associating transmission electron microscopy (TEM) with analytical techniques such as EELS and energy-dispersive X-ray spectroscopy (EDXS). A preliminary electron spin resonance (ESR) study was also performed to complete this characterization.

2. Experimental

PPP was synthesized according to the method of Kovacic and Oziomek [10]. The brown insoluble powder was washed out with water and hot hydrochloric acid to remove the catalyst residues and then was heated at 400 °C for 36 h under vacuum for further purification. Stoichiometric quantities of PPP and barium metal powders were mixed with the molar ratio $\text{C}/\text{Ba} \approx 12$ corresponding to the concentration $\text{Ba}_{0.5}(\text{C}_6\text{H}_4)$. Such a composition was previously found when heavy alkali metals were intercalated to saturation into PPP by the vapor phase method [11,12] or when the electrochemical techniques for intercalation of Li^+ , Na^+ and K^+ ions were performed [13,14]. The mixture was pressed during 3 days at room temperature in a home-made screw press at around 10–15 kbar. All these operations were performed in the high purified argon

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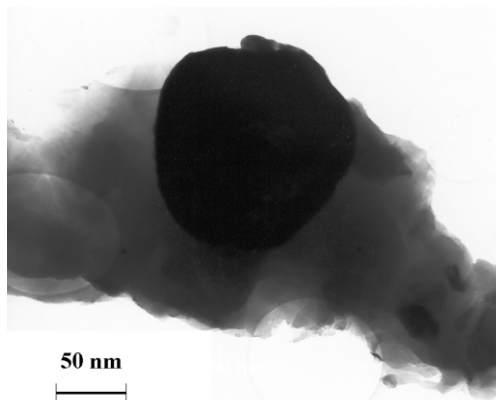


Fig. 1. TEM micrograph of a selected part of intercalated PPP.

atmosphere of a glove box. The obtained pellet was then heated under vacuum at 250 °C in a sealed glass tube in order to complete the doping reaction and to homogenize the samples. The pellet was finally ground in the glove box. The obtained powder was set in an ESR quartz tube or deposited on copper grids covered with a holey amorphous carbon layer for the TEM study. EELS studies were conducted using a GATAN 666 parallel electron energy loss spectrometer linked to a Philips CM20 Microscope working at 120 kV (unsaturated LaB₆ cathode) and connected to a Macintosh IICx microcomputer controlled by the GATAN EL/P software. The spectrometer entrance aperture, the collection half angle and the dispersion were, respectively, 2 mm, 10 mrad and 0.2 eV/channel. The energy resolution, measured at the full width at half maximum (FWHM) of the zero-loss peak is a 1.2 eV. EDX analysis was performed with an EDAX spectrometer controlled by a DX4-TEM software. The atomic concentration ratio barium over carbon Ba/C was determined in the EELS experiments by the following equation [15,16]:

$$\text{Ba/C} = I_{\text{Ba}} \sigma_{\text{C}}(\alpha, \Delta E) / I_{\text{C}} \sigma_{\text{Ba}}(\alpha, \Delta E)$$

where Ba and C are the numbers of atoms of barium and carbon per unit area, respectively, $I_{\text{Ba}}(\alpha, \Delta E)$ and $I_{\text{C}}(\alpha, \Delta E)$ are the core loss intensities integrated up to an energy of width ΔE starting at the edge onset, $\sigma_{\text{Ba}}(\alpha, \Delta E)$ and $\sigma_{\text{C}}(\alpha, \Delta E)$ are the partial ionization cross-sections integrated over the acceptance angle α and ΔE is an energy region. A typical value for ΔE in the energy region lies within 50–100 eV. The accuracy of atomic concentration ratio is lower than 10%.

ESR experiments were performed using a Bruker ER 200D spectrometer working at the microwave frequency of 9.65 GHz, with the following experimental conditions: a microwave power of 5 mW, a modulation frequency of 100 kHz and a gain of 2500.

3. Results and discussion

3.1. TEM studies

Fig. 1 shows a selected TEM micrograph typical of the samples deposited on the copper grid. It shows clearly PPP particles coexisting with an almost spherical grain of barium metal. EDX analysis carried out in various regions of different PPP particles shows that the barium content into PPP is higher in parts close to the barium particle. The Ba concentration decreased when the distance d between the analysis point on PPP and the barium metal increased (Fig. 2 displays the EDX concentration profiles at various points of the polymer). As a matter of fact, the peak related to barium decreased in intensity continuously when d increased. This indicates that the intercalation process is very inhomogeneous and depends on the contacts between the metal and the polymer particles. Chlorine, which is also evidenced with EDX analysis, is a catalyst residue of the synthesis (0.3 wt% measured by elemental analysis of the pristine polymer).

In order to characterize the phases formed during the intercalation process, EELS has been performed on various regions of the doped polymer and on the barium particle surface. Analysis was done above the holes of the grid in order to avoid the parasitic signals due to the amorphous carbon of the grid. The energy loss spectra at the M-edge of barium are displayed in Fig. 3. The spectrum of the intercalated polymer (Fig. 3(a)) exhibits two ionization edges at about 781 and 796 eV, which are typical of the barium cations. The atomic Ba/C ratios are 0.04 and 0.01, respectively, for a polymer region close to the barium grain and for the most distant one. These ratios correspond to the compositions Ba_{0.24}(C₆H₄) and Ba_{0.06}(C₆H₄). The EELS spectrum performed on the surface of the barium particle exhibits nearly the same fine structure at the M-edge of Ba than that of the doped PPP. EDX analysis (Fig. 4) reveals that the surface of barium is covered with a film of BaO (this one is certainly formed during the transfers occurring during the sample preparation). The fact that the intercalated PPP and barium oxide covering the metal particle show the same barium EELS spectra indicates that both Ba intercalated PPP and Ba engaged in the BaO film are in a +2 oxidation state.

3.2. ESR study

Fig. 5(a) shows the ESR spectrum of a powder of the PPP/Ba compound recorded at 280 K. It is composed of two signals: a narrow (linewidth peak-to-peak, $\Delta H_{\text{pp}} = 2.4$ G and $A/B = 1.7$, A and B are the intensities of the positive and negative absorption peaks, respectively) and a broad one ($\Delta H_{\text{pp}} \approx 8$ G estimated). The latter is attributed to the pristine polymer, which contains paramagnetic species related to side compounds created during the synthesis and to cross-linking macromolecules

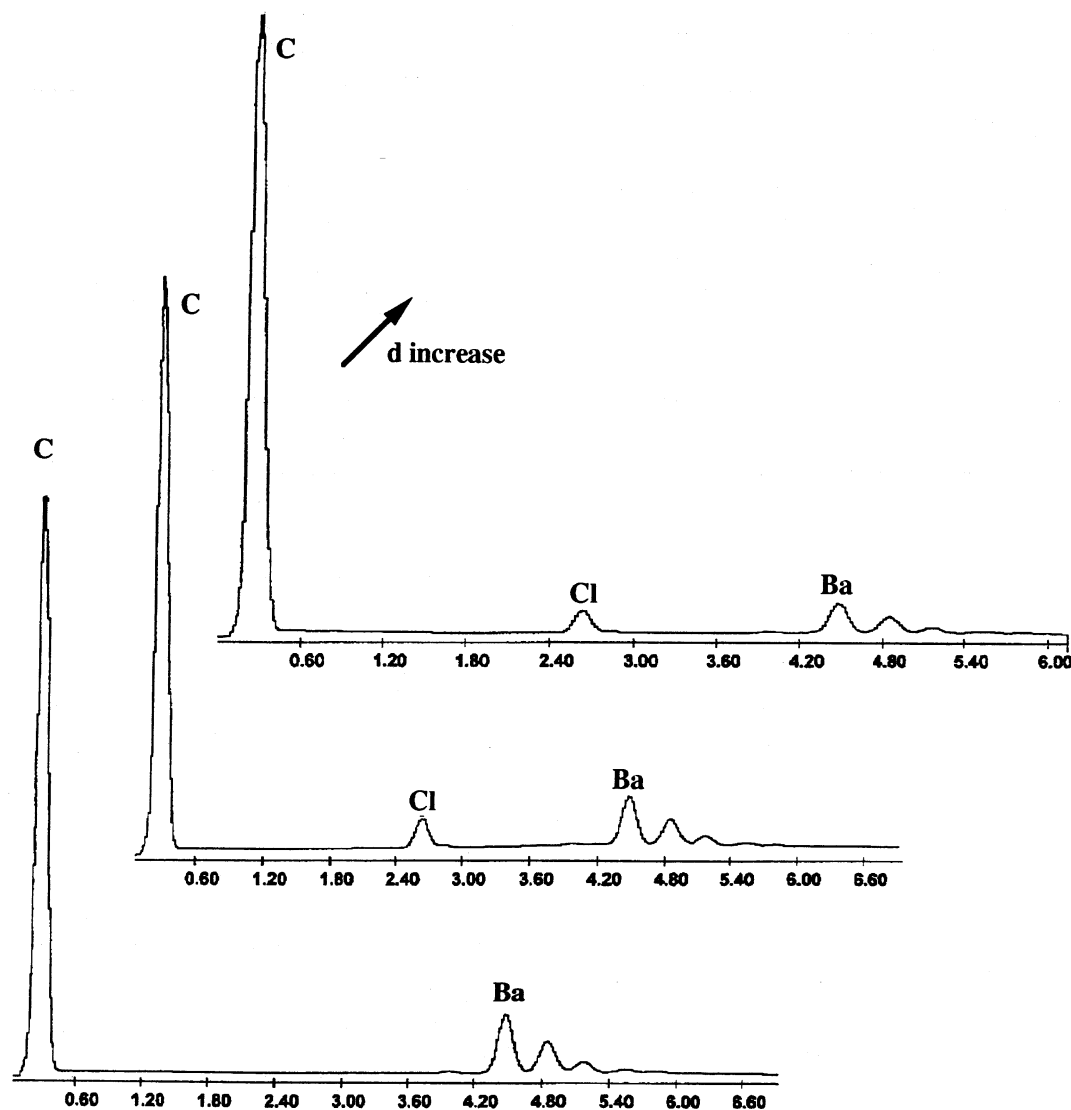


Fig. 2. EDX concentration profiles at various points on the intercalated polymer.

[5,12]. The ESR spectrum of the pristine polymer (after the annealing treatment for 36 h at 400 °C in dynamic vacuum) is displayed in Fig. 5(b) for comparison ($\Delta H_{pp} = 7.8$ G; $A/B = 1.0$). The dissymmetry of the narrow signal ($A/B = 1.7$) is unexpected because the samples are in the form of powders. Such a phenomenon, called the Dyson effect [17], is usually observed with pellets or with massive samples and is attributed to the presence of metallic regions in the sample or an inhomogeneous distribution of the microwave field. We believe that the dimensions of the polymer particles (about 100 μm for the larger ones) could induce a Dyson effect or/and the grinding of the PPP/Ba pellet to obtain the powder is unsatisfactory. In order to verify this assumption, the ESR spectrum of a pellet of the PPP/Ba compound was performed at 280 K (Fig. 5(c)). The A/B ratio of the narrow signal, which is estimated to be 2.9, increased in comparison with the Ba/PPP powder. Then,

this effect is related to the dimensions of the sample like reported by the Dyson theory.

This preliminary ESR study confirms that our experimental procedure allows the intercalation of barium ions into PPP but this insertion is very inhomogeneous and affects only a part of the polymer. Paramagnetic centers are created during the intercalation process. According to previous works [6,11,12,18], these spin centers could be attributed to paramagnetic polarons. Complementary ESR study are necessary to corroborate this attribution such as the study of the dependence of the ESR parameters (g -value, ΔH_{pp} , intensity of the signal) with the temperature. By analogy with the ESR studies of the electrochemically intercalated PPP/Na and PPP/Li compounds [19], in which the signal attributed to the polarons exhibits a linewidth ΔH_{pp} close to 2.0 G for an intermediate composition $\text{Na}_{0.3}(\text{C}_6\text{H}_4)$ and $\text{Li}_{0.3}(\text{C}_6\text{H}_4)$, the linewidth ΔH_{pp} of the narrow signal for the PPP/Ba compound is quite similar.

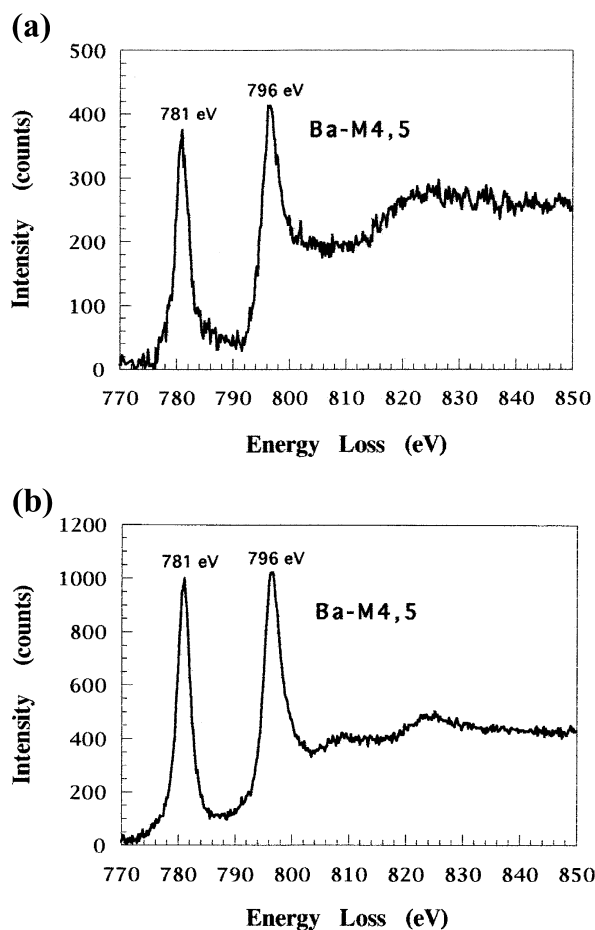


Fig. 3. EELS spectra performed on the inserted polymer (a) and barium particle surface (b).

4. Conclusion

A chemical technique using the direct reaction of the powders of barium metal and PPP allows the accommodation of barium cations into the polymer structure. Both ESR and TEM studies indicate that this intercalation affects

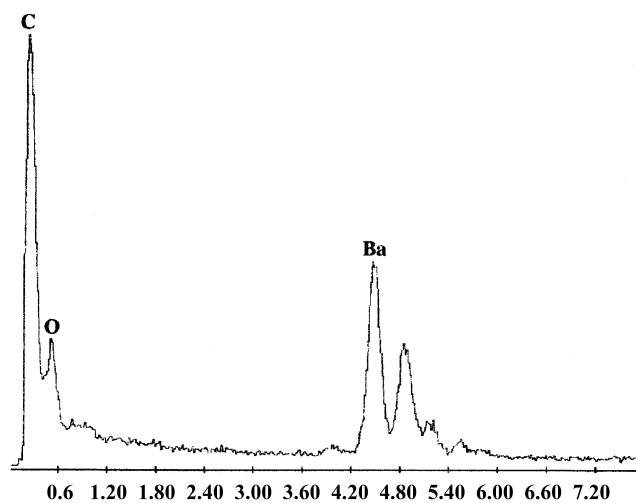


Fig. 4. EDX analysis plot of the surface of the barium particle.

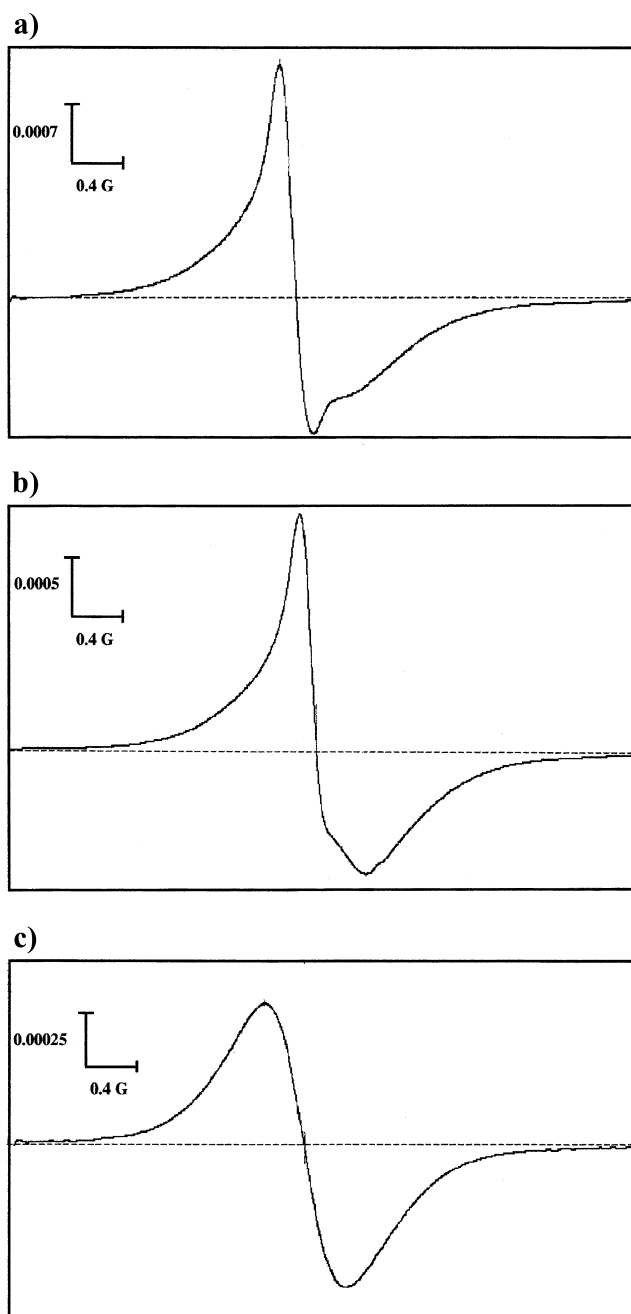


Fig. 5. Derivative of the ESR signals at 300 K of the pristine polymer (gain 5000) (a) and for PPP intercalated with barium corresponding to the powder (gain 2500) (b) and a pellet of PPP/Ba (gain 2500) (c).

only a part of the polymer. The maximum metal content was found in $\text{Ba}_{0.24}(\text{C}_6\text{H}_4)$. It is half of the value observed in alkali metal M-doped PPP and corresponding to the $\text{M}_{0.5}(\text{C}_6\text{H}_4)$ composition. Works are in progress to improve the efficiency of the doping method such as the annealing of the intercalated compound at higher temperature ($250^\circ\text{C} < T < 400^\circ\text{C}$) in order to enhance the diffusion rate of barium or successive grinding and pastilling of the samples for a better contact between metallic barium and the polymer. The EELS data seem to indicate that the

intercalated barium is in the divalent Ba^{2+} state as previously mentioned by Kaner and coworkers [7–9] related to PPP and polyacetylene reduced in doping solutions. The compressing method for the intercalation of barium into PPP can likely be extrapolated to other low vapor pressure metals like the other alkaline earth metals and some lanthanides.

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