

# Study on the Effect of Acid- or Iodine-Doping on the Properties of Copolymer C<sub>1-4</sub>Poly-Phenylene-Vinylene-Ether

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**ABSTRACT:** In this article, the new red-colored copolymer, referred to as C<sub>1-4</sub>poly-phenylene-vinylene-ether (C<sub>1-4</sub>PPV-ether) is built as a PPV polymer with some conjugated links (—CH=CH—) that are changed into ethylic-ether links (—CH<sub>2</sub>—O—CH<sub>2</sub>—) and whose modified phenyl ring is grafted, respectively, in two and five positions with methoxy and butoxy groups. The C<sub>1-4</sub>PPV-ether is doped with protonic acid or iodine. The infrared absorption (IR), optical density, X-ray photoelectron spectroscopy (XPS), and electron spin resonance (ESR) show that there is a charge transfer complex formed between the copolymer and the doping species (iodine or acidic dopants). From IR, XPS, and ESR analysis, we deduced that the doping mechanism of the copolymer is, respectively, a protonation of the double links in PPV in the case of the protonic acid doping process and a grafting of the iodine to the ether links in the case of iodine-doping process. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1858–1866, 2002

**Key words:** copolymer; dopant; ESR; XPS; CT-complex

## INTRODUCTION

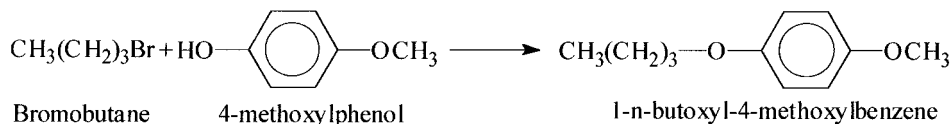
Recently, great efforts have been devoted to studying organic polymers because of their potential characteristics, such as the easy physical manipulation and the great flexibility of their chemical structure (extraction). These two characteristics allot a reasonable processing cost. One of the polymers mostly studied is polyphenylene-vinylene (PPV) because of its remarkable optical properties.<sup>1</sup> Consequently, PPV and its deriva-

tives remain suitable candidates for flexible large-area display technology based on polymer light-emitting diodes (PLEDs).<sup>2–11</sup> In parallel, a number of investigations were undertaken to ameliorate the properties of organic semiconducting polymers by doping. Therefore, much work was carried out to discover new dopants and doping techniques.<sup>12</sup> Conductor and semiconductor polymers particularly have many doping possibilities for specific applications. Many experiments were carried out by using iodine as a dopant.<sup>13–14</sup> Polymers' iodine doping results in the formation of charge-transfer complexes. Recently, it was shown that iodine can improve the performance of light-emitting diodes.<sup>15–16</sup> Furthermore, it appears that iodine is the most promising dopant

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**Scheme 1** Preparation of 1-n-butoxyl-4-methoxybenzene.

because it does not induce any degradation of the polymer<sup>14</sup> used to realize organic light emitting diodes.

After synthesizing the C<sub>1-4</sub>poly-phenylene-vinylene-ether (C<sub>1-4</sub>PPV-ether), we first focused on the classical results that indisputably proved that there is a charge-transfer (CT) complex formed between this copolymer and the dopants (iodine or acid). Then, we investigated the protocol of this CT. In an attempt to justify the formation of complex salts, our approach was to combine different techniques: electron spin resonance (ESR), X-ray photoelectron spectroscopy (XPS), infrared absorption (IR), and optical density (OD), so as to give a description of the complex salts' physical properties.

## EXPERIMENTAL

All chemicals and solvents used during the copolymer-doping process were obtained from Sigma-Aldrich Chemie S.A.R.L. (France) and Fluka Chimie GmbH (Buchs, Switzerland). Before being used, they were purified by normal procedures.

With regard to what has been said before, we have attempted to study iodine or trifluoroacetic acid-doped C<sub>1-4</sub>PPV-ether. The C<sub>1-4</sub>PPV-ether synthesis was previously described and its structure was supported by infrared measurement, Raman scattering, XPS, and optical density analysis.<sup>17</sup> To make this article easy to read, we are going to briefly recall the main stages of this copolymer synthesis. The copolymer synthesis was performed in two steps. In fact, a preparation of the monomer was followed by a copolymeriza-

tion reaction. The monomer synthesis was also carried out in two stages. First, an O-alkylation reaction consisting of fixing the bromobutane on the 4-methoxyphenol (Scheme 1) was performed. A chloromethylation reaction then followed (Scheme 2).

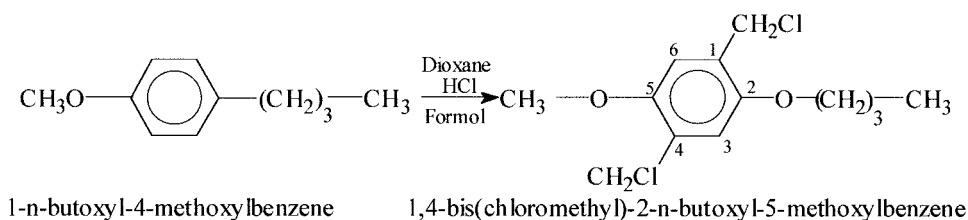
As this red-colored copolymer, the structure of which is shown in Scheme 3, is insoluble, the number of PPV monomer ( $\gamma$ ) and that of ether monomer ( $x$ ) are very difficult to determine accurately.

### Doping of the C<sub>1-4</sub>PPV-Ether Powder

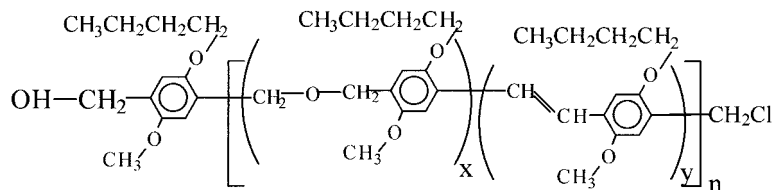
The classical method used for the C<sub>1-4</sub>PPV-ether iodine-doping is similar to that used for poly(*N*-vinyl carbazole) doping.<sup>14</sup> By using iodine (I<sub>2</sub>), the powder was placed in a separate glass cup with iodine in an isolated bell jar. The doping process was carried out at room temperature for 72 h to achieve the saturation state. In the case of protonic acid, the powder was placed for 2 h in a mixture made up of 20% of trifluoroacetic acid (CF<sub>3</sub>COOH) and 80% of acetonitrile (CH<sub>3</sub>NO<sub>2</sub>). Then the doped copolymer powder was washed three times by acetonitrile.

### Experimental Technique of Measurements

The resulting powder was characterized by XPS analysis, which was carried out at the University of Nantes-CNRS by using a Leybold LHS-12 spectrometer. The data were obtained with a magnesium radiation source (1253.6 eV) operating at 10 kV and 10 mA. The pass energy was set at 50 eV. High-resolution scans with a good signal-to-noise



**Scheme 2** Preparation of 1,4-bis(chloromethyl)-2-n-butoxyl-5-methoxybenzene.



**Scheme 3** Structure of  $C_{1-4}$ PPV-ether.

ratio were obtained in the C1s, N1s, Cl2p, O1s, F1s, and I3d regions of the spectrum. To decrease the charge effect, the powder was fixed to the substrate holder by pressing the copolymer powder onto an indium sheet. The quantitative analysis was based on the determination of the C1s, N1s, Cl2p, O1s, F1s, and I3d peak areas with sensitivity factors of 0.2, 0.36, 0.58, 0.6, 0.83, and 6.4, respectively. The sensitivity factors of the spectrometer were provided by the manufacturer. The vacuum in the analysis chamber was around  $10^{-6}$  Pa. All spectra were recorded under identical conditions. The decomposition of the XPS peaks into different components and the quantitative interpretations were made after subtraction of the background by using the Shirley method.<sup>18</sup> The developed curve-fitting programs permit the variation of parameters such as the Gaussian/Lorentzian ratio, the full width at half-maximum (FWHM), the position, and the intensity of the contribution. These parameters were optimized by a curve-fitting program to obtain the best fit.

IR and OD spectra were carried out at room temperature by using a Bruker Vector 22 spectrophotometer and a Cary 2300 spectrophotometer, respectively. For optical measurements, band po-

sitions are expressed in wave number ( $\text{cm}^{-1}$ ) from 400 to 4000 for the IR. The wavelengths, expressed in nanometers, for optical density vary from 200 to 2000. The samples were pellets of KBr mixed with the organic compound under study. ESR experiments were performed at a temperature varying from 110 to 523 K on a Bruker ER 200 D spectrometer operating at X band.

### XPS Results

As far as iodine-doping is concerned, the iodine  $I^{5-}$  line appeared at 620.0 eV<sup>15</sup> with a relative intensity equal to 6.6%. We also observe three lines (285.0, 286.3, and 288.5 eV) for C1s spectrum, respectively, attributed to C—C, C—O—C, C—O—H, or C—Cl and C=O bonds as observed in the pure sample (Table I). The same distribution was observed when doping with acid. As for the O1s spectrum, the line at 530.7 eV came from  $\text{In}_2\text{O}_3$  used as a support. The others two lines situated at 532.6 and 534.2 eV observed in pure and iodine-doped copolymer corresponded to C=O and C—O—H bonds, respectively (Table I).<sup>19</sup> We noted that the line attributed to the C=O bond disappeared in the case of acid doping but O—H was maintained. In a pure sample, the rel-

**Table I** XPS Qualitative Analysis of  $C_{1-4}$ PPV-Ether Powders Pure or Doped with Iodine or Acid

	C 1s			O 1s			Cl 2p	I 3d	N 1s		F 1s
	C—C	C—O—H C—Cl	C=O COOH	$\text{In}_2\text{O}_3$	C=O	OH	$\text{Cl}^-$	$\text{I}_5^-$	C—N	N+	
	Pure $C_{1-4}$ PPV-ether ( $\Delta E = 0.4$ )	285 <sup>a</sup> 73	286.5 23.5	288.5 3.5	529 10	531.5 25	533.1 65	200,2 100	—	—	
Iodine-doped $C_{1-4}$ PPV-ether ( $\Delta E = 0.5$ )	284.8 77	286.3 19	288.5 4	530.7 12	532.6 79	534.2 9	—	620 100	—	—	—
Acid-doped $C_{1-4}$ PPV-ether ( $\Delta E = 0.25$ )	285 73	286.5 19.5	288.5 7.5	—	—	532.4 100	—	—	398 43	400.5 57	688.9 100

<sup>a</sup> First line, binding energy after correction of the charge effect (eV); second line, relative concentration (at.%).

**Table II** XPS Quantitative Analysis of C<sub>1-4</sub>PPV-ether Powders Pure or Doped with Iodine or Acid

	C 1s	O 1s	Cl 2p	I 3d	N 1s	F 1s
Pure C <sub>1-4</sub> PPV-ether	285.43 <sup>a</sup> 84.4	533.54 15.4	200.44 0.2	—	—	—
Iodine-doped C <sub>1-4</sub> PPV-ether	284.9 82.8	532.64 16.7	199.62 0.4	620 6.6	—	—
Acid doped C <sub>1-4</sub> PPV-ether	285.3 89.2	532.5 19.9	199.8 1.1	—	399.3 1.6	688.9 3.9

<sup>a</sup> First line, binding energy (eV) before charge effect subtraction; second line, relative concentration (at.%).

ative intensity of the line attributed to C=O bond was much lower than the one observed in the case of iodine-doping sample. For the two doping processes, we noted the loss of chlorine. Then, in the case of acid doping, the N1s line grew up with two components (398.0 and 400.5 eV) attributed to C—N bonds (398.0 eV) and N<sup>+</sup> species (400.5 eV) with a relative intensity equal to 1.6%. A fluorine line corresponding to one contribution was also detected at 688.9 eV with a relative intensity equal to 3.9% (Table II).<sup>19</sup>

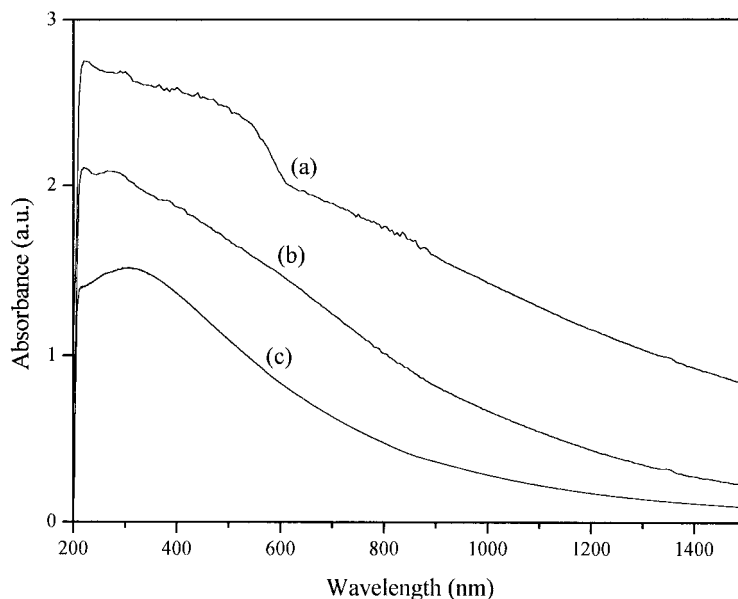
### Optical Density Measurements

Typical OD measurements can be seen in Figure 1. The results showed that whatever the dopants was, a large absorption band appeared in the domain from 200 to 800 nm. Consequently, the

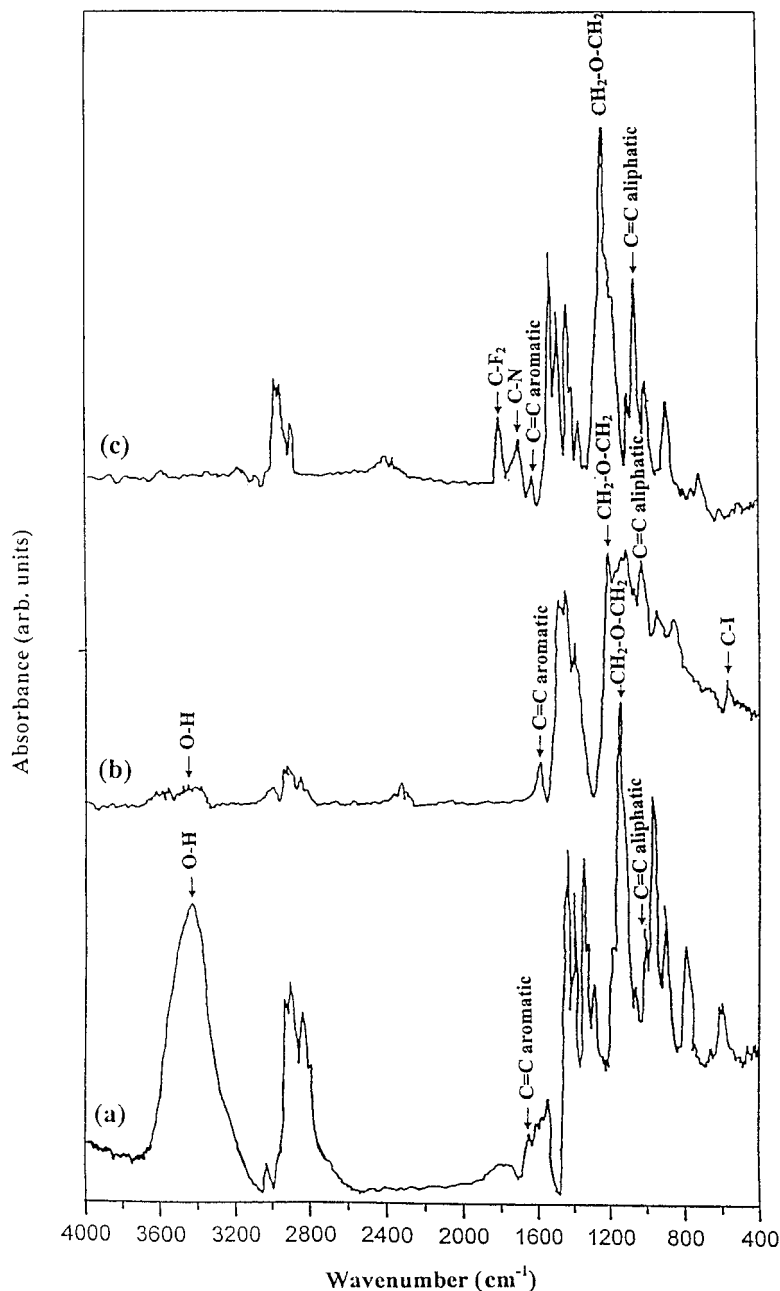
optical analysis revealed that the absorption threshold was about 2.022 eV for pure copolymer,<sup>17</sup> whereas it was 1.730 and 1.252 eV for the iodine and the protonic acid-doped samples, respectively. Furthermore, when the powder was doped with protonic acid, we could see some absorption bands had disappeared (275, 292, and 380 nm).

### Infrared Spectroscopy

We systematically studied the powder of protonic acid and iodine-doped C<sub>1-4</sub>PPV-ether. Figure 2 shows the IR spectra of pure, protonic acid and iodine-doped C<sub>1-4</sub>PPV-ether samples for some wave number varying from 400 to 4000 cm<sup>-1</sup>. By examining the results of IR, we note that the band characteristic of PPV as well as those of ether



**Figure 1** Optical density of (a) pure C<sub>1-4</sub>PPV-ether; (b) iodine-doped C<sub>1-4</sub>PPV-ether; and (c) acid-doped C<sub>1-4</sub>PPV-ether.



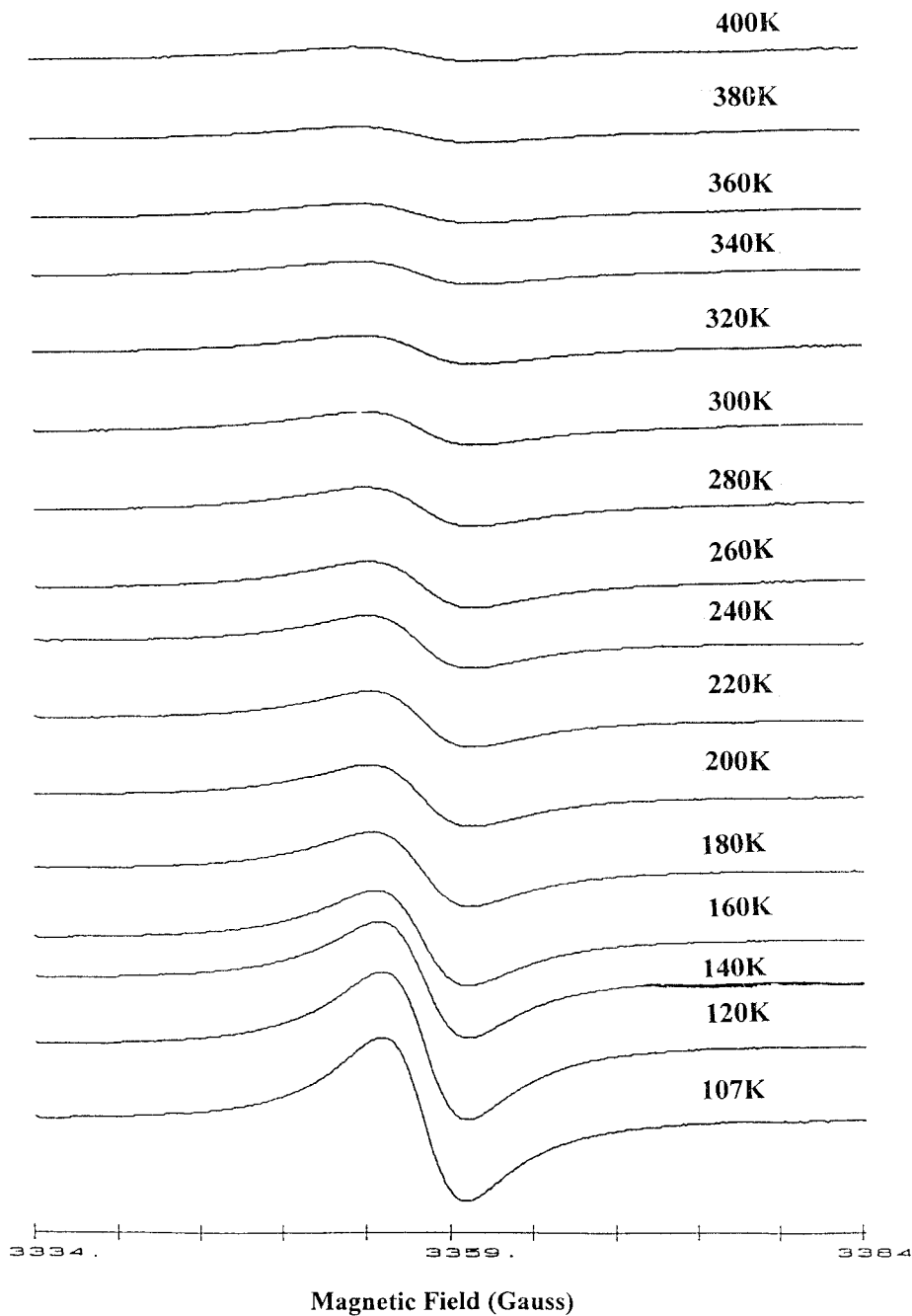
**Figure 2** IR spectra of (a) pure  $C_{1-4}$ PPV-ether; (b) iodine-doped  $C_{1-4}$ PPV-ether; and (c) acid-doped  $C_{1-4}$ PPV-ether.

function were present, which means that the copolymer structure did not change. Added to the bands attributed to PPV and the ether function, new bands appeared. In fact, we could see in Figure 2 that in the case of iodine-doped  $C_{1-4}$ PPV-ether, the new band situated at  $590\text{ cm}^{-1}$  appeared. It could be attributed to C—I vibration.<sup>20</sup> Moreover, in the case of protonic acid-doping, the band situated at  $3400\text{ cm}^{-1}$  attributed to OH

vibrations disappeared and three new bands situated at  $1776$ ,  $1679$ , and  $1463\text{ cm}^{-1}$  and, respectively, attributed to C—F<sub>2</sub>, C=N, and C—N vibrations appeared.<sup>20</sup>

### Electron Spin Resonance

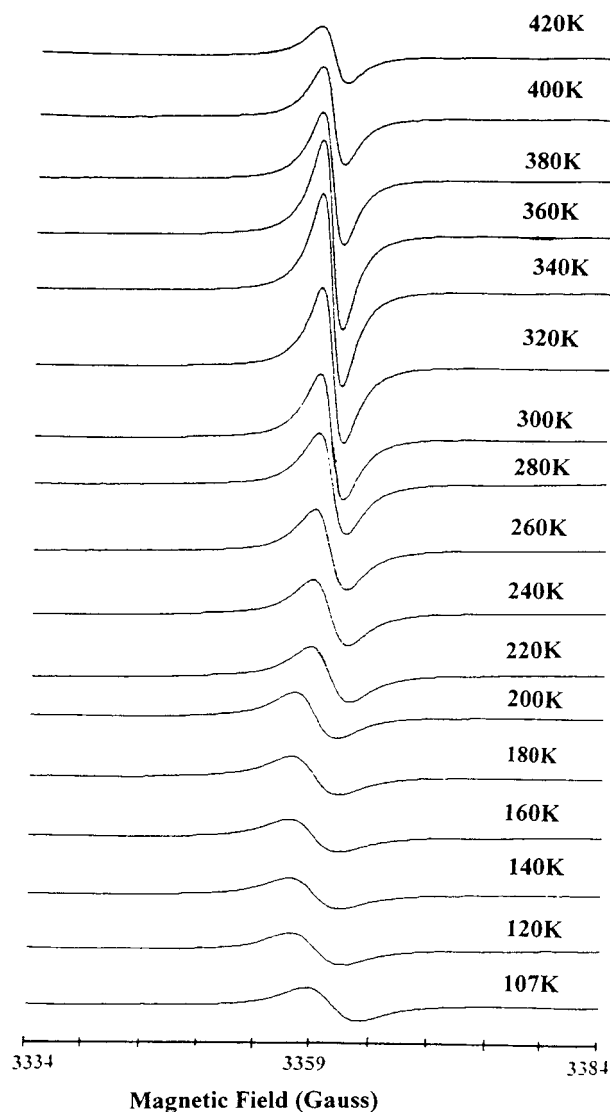
For the ESR measurements, we noted that no ESR signal was observed before doping. After



**Figure 3** Normalized ESR spectra as a function of temperature of iodine-doped C<sub>1-4</sub>PPV-ether.

doping, a well-resolved ESR signal was systematically observed. The ESR spectra of doped samples are shown in Figures 3 and 4. As can be seen, the ESR signal of iodine-doped C<sub>1-4</sub>PPV-ether at room temperature is different from that of the protonic acid-doped sample. To facilitate the understanding of the doping mechanism, we have tried to study the evolution of the relative ESR

intensity versus temperature. Results are shown in Figure 5. In the case of iodine-doping, we observed a monotonic decrease in the relative intensity of the ESR signal when the measurement temperature increases. The signal decrease could be explained by the loss of iodine from the powder. Thus, we deduced that the complex salt was not stable. In the case of protonic acid-doping, the



**Figure 4** Normalized ESR spectra as a function of temperature of acid-doped  $C_{1-4}$ PPV-ether.

relative intensity remained constant up to 240 K, which indicated that radicals were trapped in the mass of the copolymer and that not enough recombination reaction took place. The same phenomenon was observed in the case of polyethylene.<sup>21</sup> From this temperature on, we noted an increase in the relative intensity which reached the maximum of intensity at 340 K. We think that there was a thermal excitation of the radicals, so a maximum of ESR density was reached. From 340 K onward, a decrease in ESR relative intensity was observed, showing a recombination of the radicals, that is forming pair radicals without spin, which could not be detected by the ESR technique. This original behavior was reversible

and could be due to the formation of bipolarons above 340 K. However, in the case of acid-doping, the complex salt was stable.

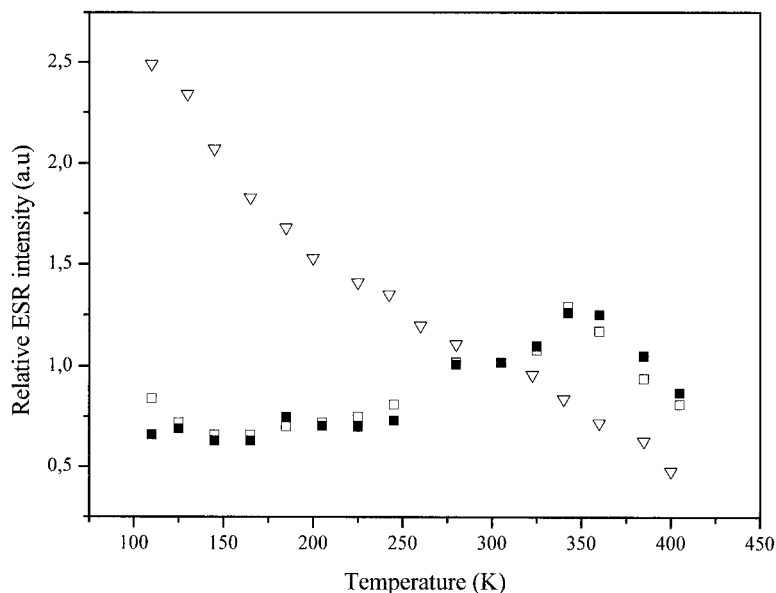
## DISCUSSION

The quantitative XPS analysis (Table II) indicated the presence of components forming  $C_{1-4}$ PPV-ether (C, O, and Cl). Furthermore, protonic acid (C, O, N, and F) and iodine components were present, which confirmed that the copolymer powder was mixed with dopants. The IR analyses revealed the appearance of new bands corresponding to C—N, C—F<sub>2</sub>, and C=N in the case of the acid-doping process and C—I in the case of iodine-doping process. We also noted the presence of a new large absorption band in the optical density. The XPS systematically showed that the dopants were in an ionic state. We could conclude that there was a formation of a CT complex between the copolymer and the dopants (iodine, protonic acid). The new large absorption band appearing in the optical density could be attributed to an absorption band of a CT complex. In addition, the appearance of ESR signals after doping confirmed that there was CT complex between the copolymer and the dopants (protonic acid, iodine), which was in accordance with the XPS, IR, and OD analyses.

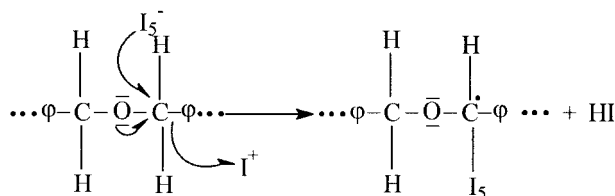
According to the ESR analyses, we could deduce that there were two different doping mechanisms. In the case of iodine-doping, the ESR studies at 300 K showed a Landé  $g$  factor value equal to 2.0026 and a value of peak-to-peak line width ( $\Delta H_{pp}$ ) equal to 7.0 G. As for acid-doping, we found the current values  $g = 2.0015$  and  $\Delta H_{pp} = 2.2$  G. These results indicated that the radical center was not the same in both cases, as shown by the XPS analyses. In fact, the  $g$  value observed for PPV radical or the radical created by irradiation in organic acid (essentially protonation of the double bond) ranged from 2.0025 to 2.0038.<sup>11,22-25</sup> Moreover, all these radicals were located on carbon atoms. In the case of organic acid, the unpaired electron was expected to reside chiefly in a  $\pi$  ( $2p_z$ ) state on the carbon atom of the carboxyl group where the  $z$  direction is normal to the plane of the group. The smallest principal value of the  $g$  tensor was expected to be close to the free-spin value (2.0023) and the corresponding principal axis should be in the  $z$  direction.<sup>26,27</sup>

The iodine-doping process was focused on the ether bands with the linking of  $I^{5-}$  to the C—O—C band (Scheme 4).



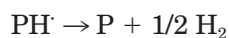
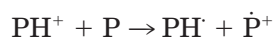
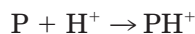


**Figure 5** Variation of normalized ESR under temperature in iodine-doped C<sub>1-4</sub>PPV-ether (▽), acid-doped C<sub>1-4</sub>PPV-ether (□), and acid-doped C<sub>1-4</sub>PPV-ether after 8 days (■).



**Scheme 4** Iodine doping.

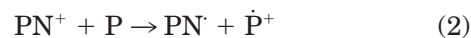
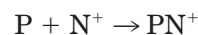
However, in the case of the protonic acid doping process, we think that the doping mechanism of the copolymer was a protonation of the double links of the PPV part. The acid protonation could begin by this first step:



**Scheme 5** Acid doping.

The  $\dot{\text{P}}^+$  radical could react with  $\text{F}^-$  ions present in the solution

We could also have a production of  $\text{P}^+$  radical by the reaction



If the probability of eqs. (1) and (2) is the same, the number of PF radicals should be the double. In fact, the XPS analyses showed that the fluorine content (3.9%) was slightly more than the double nitrogen content (1.6%).

## CONCLUSION

As shown by the XPS, OD, IR, and ESR measurements, a complex salt was formed between the copolymer and the dopants (protonic acid, iodine). Thus, the results show that there are two different doping mechanisms: time stable protonation of the double links in PPV in the case of the protonic acid-doping process, and an unstable grafting of iodine to the ether links in the case of iodine-doping process. It should be interesting to stabilize the iodine-doping by annealing treatment and to study



the evolution of the protonic acid doping in accordance with time. In this context, extensive efforts are underway in our laboratory.

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## REFERENCES

1. Nguyen, T. P.; Molinié, P.; Destruel P. in *Handbook of Advanced Electronic and Photonic Materials and Devices V10: Light-Emitting Diodes, Lithium Batteries, and Polymer Devices*; Nalwa, H. S., Ed.; Academic Press: San Diego, 2001; p 1.
2. Burrows, P. E.; Bulovic, V.; Gu, G.; Kozlov, V.; Forrest, S. R.; Thompson, M. E. *Thin Solid Films* 1998, 331, 101.
3. Roth, S.; Burghard, M.; Leising, G. *Curr Opin Solid State Mater Sci* 1998, 23, 209.
4. Heeger, A. J. *Solid State Commun* 1998, 107, 673.
5. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* 1999, 397, 121.
6. Son, S.; Lovinger, A. J.; Galvin, M. E. *Polym Mater Sci* 1995, 72, 567.
7. Miao, Y. P.; Bazan, G. C. *J Am Chem Soc* 1994, 116, 9379.
8. Shah, H. V.; McGhie, A. R.; Arbuckle, G. A. *Thermochem Acta* 1996, 287, 319.
9. Greiner, A.; Heitz, W. *Makromol Chem Rapid Commun* 1998, 9, 581.
10. Lenz, R. W.; Han, C. C.; Stenger-Smith, J.; Karasz, F. E. *J Polym Sci, Polym Chem Ed* 1998, 26, 3241.
11. Nguyen, T. P.; Le Rendu, P.; Tran, V. H.; Molinié, P. *Polym Adv Technol* 1998, 9, 101.
12. Baughman, R. H.; Bredas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem Rev* 1982, 82, 209.
13. Safoula, G.; Bernède, J. C.; Alimi, K.; Molinié, P.; Touhri, S. *J Appl Polym Sci* 1996, 60, 1733–1739.
14. Alimi, K.; Safoula, G.; Bernède, J. C.; Rabiller, C. *J Polym Sci, Part B: Polym Phys* 1996, 34, 845–851.
15. Romeo, D. B.; Schaer, M.; Zuppiroli, L.; Cesar, B.; François, B. *Appl Phys Lett* 1995, 67 (18), 1659.
16. Huang, F.; MacDiarmid, A. G.; Hsieh, B. R. *Appl Phys Lett* 1997, 71 (17), 2415.
17. Alimi, K.; Molinie, P.; Blél, N.; Fave, J. L.; Bernède, J. C.; Ghedira, M. *Synth Met to appear*.
18. Shirley, D. A. *Phys Rev B* 1972, 5, 4709.
19. Beamson, G.; Briggs, D. in *High-Resolution XPS of Organic Polymers; The Scienta ESCA 300 Database*; John Wiley and Sons: Chichester, 1993.
20. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press Harcourt Brace Jovanovich: New York, 1989.
21. Legeay, G.; Rousseau, J. J.; Brosse, J. C. *Eur Polym J* 1985, 21 (1), 1–7.
22. Nguyen, T. P.; Giffart, M.; Molinié, P. *J Chem Phys* 1994, 100 (11), 8340.
23. Kuroda, S.; Murase, I.; Ohnishi, T.; Noguchi, T. *Synth Met* 1987, 17, 663–666.
24. *Electron Spin Resonance and the Effects of Radiation on Biological Systems*; Nuclear Sciences Series Report Number 43; Snipes, W., Ed.; National Academy of Sciences: Washington, DC, 1968, p 123.
25. Fujimoto, M. *J Chem Phys* 1963, 39, 846.
26. Box, H. C.; Freund, H. C.; Budzinski, E. E. *J Chem Phys* 1968, 49, 3974.
27. Cole, T.; Heller, H. C. *J Chem Phys* 1965, 42, 1668.