

Conducting Properties of Iodine-Doped Low-Density Polyethylene–Poly(4-Vinylpyridine) Blends

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ABSTRACT: The conductivities of blends of low-density polyethylene and poly(4-vinyl pyridine) (P4VP) were studied. The blends were synthesized by *in situ* sorption and thermal polymerization of 4-vinylpyridine in low-density polyethylene. They showed, after iodine doping, conductivities of 1.7 to $5.0 \times 10^{-7} \text{ S cm}^{-1}$ at 298 K, depending on the P4VP mass increment into the matrix. Their conductivities were one order of magnitude higher for measurements at

338 K. The optimum ratio of iodine to pyridine (n) which gave the highest conductivity was 0.21. The thermal stability of doped blends was acceptable for their uses as electrochemical devices. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 939–944, 2003

Key words: conducting polymer blends; iodine doping; poly(4-vinyl pyridine); low-density polyethylene

INTRODUCTION

In general, most polymers are insulating because they possess low conductivity. The conductivity depends on the thermally generated carriers and also on the addition of suitable dopants.^{1,2}

Because of the complexity of the chemical and physical structures of polymers, the role of dopants in the conduction process is not well understood.³ However, a considerable amount of work has been reported on steady-state electrical conduction in impurity-doped polymers.^{4–6} The introduction of a dopant into a polymer can considerably modify the charge storage property of the polymer or it can improve the charge carrier mobility.^{1,7} Many of the presently available doped conductive polymers possess some undesirable characteristics such as environmental instability, poor processibility, or poor physical properties. Attempts have been made to improve the physical properties of these conductive polymers.

A large number of studies have been carried out with the objective of preparing microphased polymer systems, in the form of either blends or block/graft copolymers. One of the phases is formed by a polymer capable of being doped to achieve electrical conductivity, and the second phase, by a polymer segment or a host matrix capable of improving the mechanical

and thermal properties of the conducting structure.^{8–10}

It is known that poly(4-vinylpyridine) (P4VP) doped with iodine results in an electronic semiconductor.¹¹ Block copolymers based on P4VP and poly(dimethyl siloxane) (PDMS) have been reported in the literature.⁹ The presence of an isolating PDMS segment in these materials does not greatly affect the conductivity but it does improve the physical properties of the conducting system.

Blends of low-density polyethylene (LDPE) and P4VP have been prepared.¹² They are synthesized by *in situ* by sorption of 4-vinylpyridine (4VP) followed by thermal polymerization. LDPE was chosen as the P4VP host matrix because of its ready availability as a film and its good mechanical properties. The same method has been used to synthesize LDPE/poly(acrylic acid) and LDPE/poly(methyl methacrylate).^{13,14} The blends exhibit new properties such as ion exchange, ionic conduction, and fluorescence.^{15–17}

This work details our findings concerning the changes that occur in the properties and structure of LDPE/P4VP blends upon iodine doping.

EXPERIMENTAL

Characterization of LDPE films

LDPE sheets [$d = 0.918 \text{ g/cm}^3$, melt index = 1.15 g/min] were supplied by Poliolefinas (São Paulo, SP, Brazil).

The films ($3 \times 4 \text{ cm}$) were cleaned and the characteristics of polymer checked by FTIR spectroscopy.¹³ The degree of crystallinity was 50% as measured by X-ray diffraction.¹⁸

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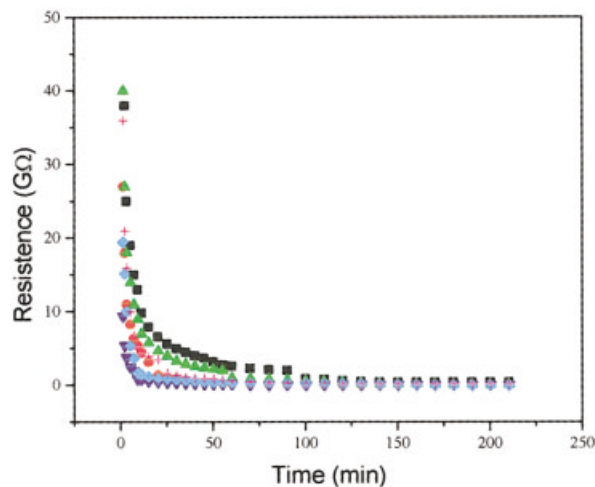


Figure 1 Resistance versus iodine doping time of LDPE/P4VP blends. Mass increase: 56% (■); 82% (●); 100% (▲); 137% (▼); 161% (◆); 208% (+). Temperature: 298 K.

Sorption and thermal polymerization of 4VP in LDPE films

The sorption and *in situ* thermal polymerization of the monomer (4VP) in LDPE matrix followed the procedure described elsewhere.¹² FTIR spectrophotometer (Michelin Bomen Hartman and Braun series MB) was used to check the occurrence of 4VP polymerization into the matrix.

P4VP mass increment into LDPE matrix was calculated gravimetrically.

Conductivity measurements

Conductivity measurements followed the procedure described by Frisch and de Barros.¹⁹ Clean samples were fixed in a glass cell and two platinum wires were attached to the film by using an Electrodag 502 paste. Vapor-phase iodine doping was used. The resistance of the film was monitored periodically with iodine uptake, at high vacuum, until the film was saturated with iodine. A Keithley 617 digital electrometer was used for the measurements. The conductivity was calculated by using the values of resistance, distance between electrodes, and cross area of the film.

The iodine mass incorporated into a blend at saturation was calculated gravimetrically followed by the molar ratio (n = moles of iodine atom/moles of pyridine units).

The Raman spectroscopy measurements

The Raman spectra were acquired on a Renishaw Raman System 3000 equipped with an Olympus microscope with a 50 \times objective. As exciting radiation, the 632.8-nm line from an He-Ne (Spectra Physics) laser was used.

Thermal measurements

DSC measurements were carried out by use of a SHIMADZU DSC 50 calorimeter. Experiments were conducted at a temperature range of 173 to 453 K and at a scanning rate of 10 K/min in a helium atmosphere. Sample amounts of 5–10 mg were used. The glass transition temperature (T_g) values of the materials were obtained from the second-run DSC curve. The thermal stability of the samples was investigated by using a SHIMADZU TG 50 instrument at a scanning rate of 20 K/min in a helium atmosphere. Sample amounts of 5–10 mg were used.

RESULTS

Conductivity measurements

The samples, after *in situ* sorption and thermal polymerization of 4VP in LDPE, showed FTIR bands characteristic of pyridine ring and none insaturation, which confirmed the monomer polymerization into the matrix. The resistance of samples, fixed in appropriate cell as described under Experimental, was monitored for iodine doping time.

Figure 1 shows the resistance of samples versus iodine doping time at 298 K. An exponential decay of resistance with time was observed. The resistance reached a constant and minimum value from 15 to 50 min of iodine exposure (mass increments: 56–250%). Table I summarizes the conductivity at iodine saturation.

TABLE I
Characteristics and Conductivities of LDPE/P4VP Blends

Sample (no.)	Mass increment (%)	Molar ratio at saturation n -(iodine moles/pyridinic units moles)	Conductivity	
			(10^{-7} S cm^{-1}) 298 K	(10^{-6} S cm^{-1}) 338 K
S ₁	56	0.08	1.7	0.74
S ₂	82	0.09	2.5	1.16
S ₃	100	0.11	3.3	2.25
S ₄	137	0.18	5.7	2.85
S ₅	161	0.21	8.0	3.11
S ₆	208	0.25	3.3	0.97
S ₇	250	0.27	3.1	0.97

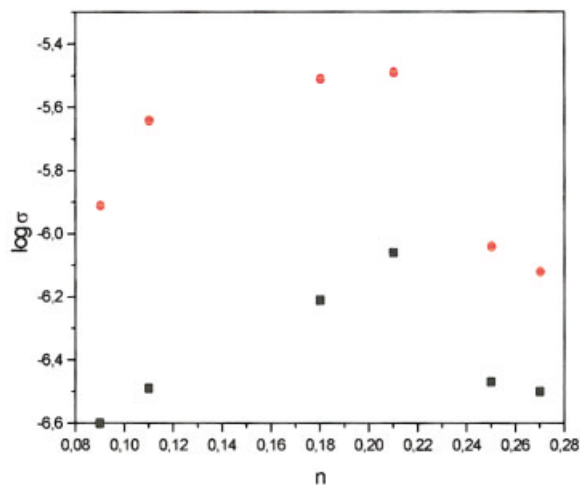


Figure 2 $\log(\text{conductivity})$ versus molar ratio (n) of LDPE/P4VP blends. Temperature measurements: (a) 298 K (■); (b) 338 K (●).

tion time measured at 298 and 338 K. After saturation, the conductivity was eight to nine orders of magnitude higher than for those undoped blends ($\sigma = 10^{-15}$ S cm^{-1}), depending on the temperature. The molar ratio (n) of iodine and pyridine units at saturation varied from 0.08 to 0.27, depending on P4VP mass increment into the LDPE matrix (Table I).

The plot of $\log(\sigma)$ versus n at 298 and 338 K is shown in Figure 2. A linear behavior of $\log(\text{conductivity})$ for the n value up to 0.21 (mass increment of 161%) was observed [Fig. 2(a)]. However, the $\log(\sigma)$ conductivity at 338 K showed anomalous behavior for increasing σ values up to 3.11×10^{-6} S cm^{-1} ($n = 0.21$) [Fig. 2(b)]. The anomalous behavior could be associated with iodine desorption of samples. For higher molar ratios ($n > 0.21$), a decrease of conductivity was observed at both temperatures. Similar results were found in the literature.⁹

Studies of the temperature effect on the conductivity of samples were conducted. Figure 3 shows the plot of $\log(\sigma)$ versus $(1/T)^{1/2}$ for samples S_1 to S_5 ($n = 0.08$ to 0.21). Linear behavior over the temperature range of 268–298 K was observed. A deviation from linearity occurred for measurements at temperatures above 298 K, which could be associated with the entropy contribution effect on the electric charge mobility into the samples.

The films became flexible after doping, suggesting a plasticizing effect of iodine into the blends.

The Raman spectroscopy of LDPE/P4VP films before and after doping

For better understanding of conduction mechanism, the Raman spectra of samples S_3 (100% of mass increase) and S_4 (137% of mass increase), before and after the doping process, were obtained (Fig. 4). The

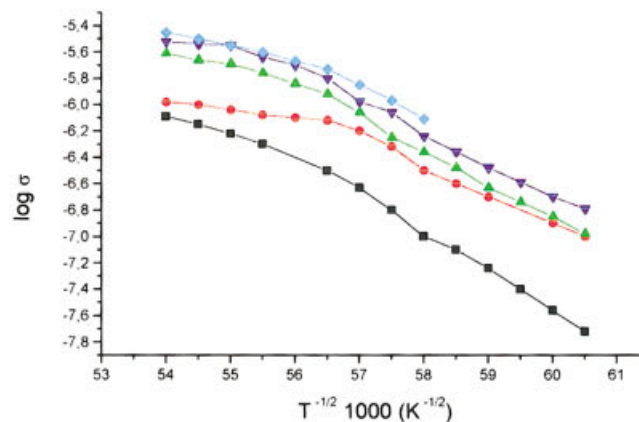


Figure 3 $\log(\text{conductivity})$ versus $(1/T)^{1/2}$ of doped LDPE/P4VP blends. Molar ratio (n): (a) 0.08 (■); (b) 0.09 (●); (c) 0.11 (▲); (d) 0.18 (▼); (e) 0.21 (◆).

sample S_4 (undoped) showed a broad band in the region of 100–700 cm^{-1} due to fluorescence of LDPE matrix as previously reported¹⁷ [Fig. 4(a)]. The Raman spectrum of the same sample after doping ($n = 0.18$) showed two clear bands [Fig. 4(b)]: one at 110 cm^{-1} , assigned to symmetric stretching of I_3^- , and the second at 167 cm^{-1} , identified as stretching of I_5^- , respectively.²⁰ The intensity ratio between the bands was 1 : 1, indicating similar concentrations of the two ion species in doped material.^{20,21} Figure 4(c) shows the Raman spectrum of a sample containing a lower amount of P4VP in the matrix (100% of mass increase, S_3) after doping ($n = 0.11$). It showed a similar pattern as that before. However, the intensity ratio between the bands was $\sim 1 : 3$. This indicates a higher concentration of long-chain polyiodides was formed in the modified matrix containing a lower amount of P4VP.

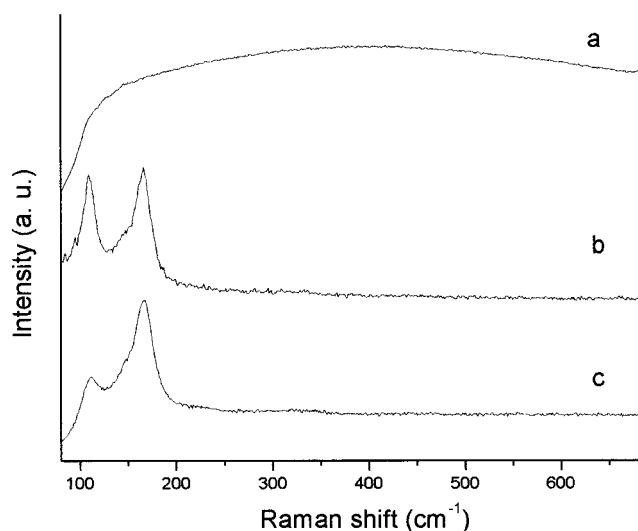


Figure 4 Raman spectrum of LDPE/P4VP blend. (a) Mass increase = 137%, $n = 0.18$; (b) after iodine doping: mass increase = 137%, $n = 0.18$; (c) after iodine doping: mass increase = 100%, $n = 0.11$.

TABLE II
DSC Data for LDPE/P4VP Blends

Sample (no.)	$[(W - W_o)/W_o] \times 10^2$	T_g (K)					
		Undoped			Doped		
		I	II	III	I	II	III
S ₁	56	264	a	420	267	286	425
S ₂	82	265	a	425	267	281	423
S ₃	100	264	a	425	268	280	424
S ₄	137	268	288	425	267	286	425
S ₅	161	286	339	426	279	287	423
S ₆	208	261	303	423	269	282	428
S ₇	250	280	313	425	288	311	424

^a Transition of difficult identification.

Thermal stability studies

The T_g values of LDPE/P4VP materials before and after iodine doping were obtained from DSC curves (Table II). Two or three T_g values were found before and after iodine doping. The two transitions, in between the T_g values of pure components [$T_{gLDPE} = 197$ K²² and $T_{gP4VP} = 423$ K⁹], and named T_g (I) and T_g (II), were identified as being due to microdomains of the blends. The third, T_g (III), was identified as due to pure P4VP segments in the blend. A thermal transition at low temperature, which would correspond to the T_g of pure LDPE domains, could not be observed. For high P4VP mass increments (S₄ to S₇), three T_g values, for each undoped and doped sample, were observed. The first and second glass transitions [T_g (I) and T_g (II)] were much broader depending on P4VP mass increment. This effect may be associated with the formation of smaller microdomains in blends, indicating partial miscibility of the two polymer components. In some cases, the second glass transition, [T_g (II)], of doped samples (S₅ to S₆) decreased as compared to that of undoped (Table II). This fact might be an indication of the plasticizing effect of iodine or/and the result of partial degradation of pure P4VP, due to the reaction of iodine with P4VP into the blends, also observed in literature.^{8,9} In this case, partial miscibility of the polymer components would occur by low-molecular-weight fractions of pure P4VP, which diffuse into the microdomains of the blend. The first and third transi-

tions, [T_g (I) and T_g (III)], kept approximately the same values for each doped and undoped sample.

The decomposition temperatures of doped blends are assigned in Table III. Two or three decomposition steps were observed. The first, more evident for higher amounts of P4VP, was assigned as being due to I₃⁻ and I₅⁻ ion degradation ($T_{dmax} = 385$ K; $T_{dmax} = 392$ K).²³ The second was identified as being due to degradation of P4VP chain segments.²⁴ These values were inferior to those of undoped blends (Table IV). The third decomposition step was attributed to LDPE chain degradation.²² In this case, the maximum decomposition temperature (T_{dmax}) was 4–40 K higher than that of the undoped blend.

DISCUSSION

The blends synthesized by *in situ* sorption and thermal polymerization of 4VP showed low conductivity ($\sigma = 10^{-15}$ S cm⁻¹). The introduction of a dopant into the system modified considerably the charge storage property of the blends increasing their conductivities by eight orders of magnitude (1.7 to 5.0×10^{-7} S cm⁻¹) at room temperature. The conductivity of samples increased one order of magnitude for measurements at 338 K (0.74 to 3.11×10^{-6} S cm⁻¹). The conductivities of doped materials reached a maximum at molar ratio of 0.21 ($n = \text{moles I}/\text{moles pyridine}$)

TABLE III
Thermal Data for Doped LDPE/P4VP Blends

Sample (no.)	$[(W - W_o)/W_o] \times 10^2$	T_{di} (K)			T_{dmax} (K)			T_{df} (K)		
		I	II	III	I	II	III	I	II	III
S ₁	56	330;	590;	745	382;	621;	761	431;	647;	774
S ₂	82		610;	742		635;	761		658;	777
S ₃	100	325;	606;	747	385;	636;	763	460;	665;	775
S ₄	137	330;	582;	737	392;	643;	756	467;	682;	770
S ₅	161		555;	723		658;	772		706;	794

TABLE IV
Thermal Data for Undoped LDPE/P4VP Blends

Sample (no.)	$[(W - W_0)/W_0] \times 10^2$	T_{di} (K)	T_{dmax} (K)	T_{df} (K)
PEBD ^a	—	754	774	804
P4VP ^b	—	653	688	723
S ₁	56	694	726	755
S ₂	82	687	721	752
S ₃	100	674; 735	700; 755	718; 770
S ₄	137	677; 715	700; 752	728; 770
S ₅	161	684; 736	706; 754	722; 766

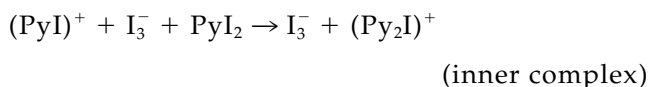
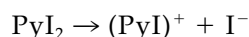
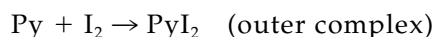
^a Ref. (22).

^b Ref. (24).

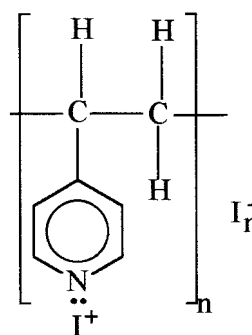
units). Similar results were also reported in the literature.⁹ The decrease of conductivity for higher molar ratios (>0.21) may be explained by the partial miscibility of the polymer components into the matrix, which would be a consequence of the iodine reaction with P4VP yielding low-molecular-weight fractions of pure P4VP, which diffuses into microdomains of the blend. If so, the P4VP-I₂ phase would be diluted and its conductivity might be reduced.⁸

The microphased domains of the materials were confirmed by the three T_g values. The decrease of T_g (II) of two samples (S₅ and S₆), containing high amounts of P4VP, after doping might be evidence of the plasticizing effect of iodine and/or partial degradation of pure P4VP segments, also reported by Nugay et al. for block copolymers containing P4VP segments.⁹ Although the homopolymer P4VP and LDPE/P4VP are extremely brittle materials, doped LDPE/P4VP blends are ductile.

The following reactions have been suggested to occur between pyridine groups of P4VP phase into blend and I₂^{9,25}:



It is generally accepted that P4VP can form a charge transfer complex with iodine similar to that found with P2VP.²⁶ This has been confirmed by the Raman spectroscopy studies indicating the conduction mechanism by I₃⁻ and I₅⁻ species in doped samples. The following structure is proposed:



Also, the evolution of iodine in doped LDPE/P4VP has been observed in most the samples by thermal analysis in the literature.²³

The stability of doped materials is acceptable for the proposed use.

Finally, the introduction of a dopant into LDPE/P4VP blends considerably modified the charge storage performance of these phase-separated materials, which can be potentially useful for electrochemical devices.

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References

1. Mehendru, C.; Pathak, N. I.; Jain, K.; Mehendru, P. *Phys Stat Sol A* 1977, 42, 407.
2. Shinka, H. C.; Talwar, I. M.; Srivastava, A. P. *Thin Solid Films* 1989, 82, 229.
3. Connel, R. A.; Gregor, L. V. *J Electrochem Soc* 1986, 112, 1198.
4. Krare, P.; Srivastava, A. P. *Ind J Pure Appl Phys* 1991, 29, 410.
5. Sharma, A. K.; Rukumini, B. *Br Polym J* 1990, 22, 39.
6. Frommer, J. E. *Acc Chem Res* 1986, 19, 2.
7. Davies, D. K. *J Phys D: Appl Phys* 1972, 5, 162.
8. Möller, M.; Lenz, R.W. *Makrom Chem* 1989, 190, 1153.
9. Nugay, N.; Küçükyavuz, Z.; Küçükyavuz, S. *Polymer* 1994, 35 (2), 243.
10. Galvin, M. E.; Wnek, G. E. *Polym Commun* 1982, 23, 795.
11. Khan, I. M. *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I. Ed.; John Wiley and Sons: New York, 1990.
12. de Barros, G. G.; Sales, M. J. A.; de Britto, A. R. F. *Polym Eng Sci* 1996, 36 (8), 1125.

13. Sales, M. J. A.; de Barros, G. G. *J Appl Polym Sci* 1993, 47, 1395.
14. Sales, M. J. A.; de Barros, G. G. *Polym Bull* 1996, 36, 495.
15. Ximenes, M. I. N.; Serra, O. A.; de Barros, G. G. *Polym Bull* 1992, 28, 61.
16. Ximenes, M. I. N.; Serra, O. A.; de Barros, G. G. *Polym Bull* 1993, 30, 97.
17. Sales, M. J. A.; Serra, O. A.; de Barros, G. G. *J Appl Polym Sci* 2000, 78, 919.
18. Aggarwal, S. L.; Tilley, G. P. *J Polym Sci* 1955, 18, 17.
19. Frisch, H. L.; de Barros, G. G. *J Polym Sci, Part A: Polym Chem* 1992, 30, 937.
20. Forsyth, M.; Shriver, D. F.; Ratner M. A.; DeGroot, D. C.; Kannewurf, C. R. *Chem Mater* 1993, 5, 1073.
21. zur Loye, H. C.; Heyen, B. J.; Marcy, H. O.; DeGroot, D. C.; Kannewurf, C. R.; Shriver, D. C. *Chem Mater* 1990, 2, 603.
22. Sperling, L. H. *Introduction to Physical Polymer Science*; John Wiley and Sons: New York, 1987.
23. Zeng, X. R.; Ko, T. M. *J Polym Sci, Part B: Polym Phys* 1997, 35, 1993.
24. Kairou, K. S. *Polym Deg Stab* 1994, 46, 315.
25. Sakai, H.; Matsuyama, T.; Maeda, Y.; Yamaoka, H. *J Chem Phys* 1981, 75 (10), 5155.
26. Stankovic, R. I.; Lenz, R. W.; Karasz, F. E. *Eur Polym J* 1990, 26 (3), 359.