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Ionic conductivity of swollen LDPE/poly(4-vinylpyridine) blend

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Summary

LDPE/P4VP films synthesized by *in situ* sorption and thermal polymerization of 4-vinylpyridine, (4VP), were used for conductivity investigations. The conductivities of swollen films varied from $7x10^{-6}$ to $1.21x10^{-3}$ $S.cm^{-1}$ at room temperature depending on P4VP mass increase in the host matrix. For the temperature range of 303-333K the conductivity varied from $7x10^{-6}$ to $2.66x10^{-3}$ $S.cm^{-1}$. A comparison between Arrhenius and VTF plots for conductivity measurements showed a best fit for temperature dependence according Arrhenius modified equation. The materials are stable for temperatures below 645 K.

Introduction

Ionic conductivity in polymers has been of interest in the research due to special applications of these materials as batteries or fuel cells. The prerequisite for good ionic conductivity is deliberate addition of ions into an environment that allows a high mobility. Some examples show how ions can usually be introduced into polymers (1).

The solvent-swollen polyelectrolytes have long been recognized as excellent protonic conductor (2). Water-containing Nafion in the proton form at room temperature reaches a conductivity of 10^{-2} $S.cm^{-1}$. These materials conduct better with higher water content and probably the proton motions are similar to those in systems of sorbed water than to ionic conduction in solvent-free polymer electrolytes (2,3).

Structural polymers are often based on polymer blends to achieve good mechanical properties. In these materials the two polymers involved in the blend exist as a physical mixture of separate phases held together by physical forces and not by chemical bonds. Investigations of polymers blends as electrolytes have been carried out mainly to improve the structural characteristics of polymer electrolytes (4).

Blends of low density polyethylene (LDPE) and poly (4-vinylpyridine), P4VP, have been prepared (5). They are synthesized by *in situ* sorption of 4-vinylpyridine in LDPE films followed by thermal polymerization. LDPE was chosen as host matrix because of its ready availability as a film and good

mechanical properties. These materials showed broad glass transitions indicating, eventually, some degree of phase separation (5). The same method have been used to synthesize LDPE/ poly(acrylic acid), PAA (6,7) . The films of modified LDPE/PAA exhibited ion exchange and fluorescence properties.
In this work, an investigation of conductivity mechanisms of LDPE/P4VP films have been carried out, looking forward an understanding of their structure-properties relationships for optimizing them as electrochemical polymer-blends devices.

Experimental

Materials

Low density polyethylene sheets (LDPE, d= 0.918 g/cm^3, MI= 1.15 g/min) were supplied by Poliolefinas (São Paulo). The films (3x4 cm and 280 µm thick) were cleaned and characterized as described previously (7).4-Vinylpyridine (4VP) was supplied by Aldrich Chem. Co..All reagents were of analytical grade and used without further purification.

Methods

Sorption and Thermal Polymerization of 4VP in LDPE Matrix

The sorption and *in situ* thermal polymerization of 4VP in LDPE matrix followed the procedure described elsewhere (5).LDPE films were immersed in 95% 4VP (containing 100 ppm of hidroquinone) under nitrogen atmosphere at 353K and specific reaction time. After sorption, the samples were rinsed in 1:1 water/ethanol solution and dried under reduced pressure (1 torr). The mass increase of LDPE films was obtained gravimetrically:

$$\%\ \text{mass increase} = [(W - W_o)/\ W_o]\ .\ 10^2$$

where,
W = mass of LDPE film after monomer sorption and thermal polymerization;
W_o = initial mass of LDPE film.

FTIR spectroscopy (Michelin Bomen Hartman & Braun series MB) was used to check the 4VP polymerization into matrix.

Swollen of LDPE/P4VP Films

LDPE/P4VP films were swollen in H_2O (333K, 48h) followed by immersion in 1M $HClO_4$ solution (333K, 72h).

Conductivity Measurements

Conductance measurements were realized using a electrolytic cell adapted to a conductimeter (Electrometer Keithley mod.617). The swollen films were cut out into disks (2.3 cm^2) and fixed between the platinum electrodes (1.06 cm^2)

of the electrolytic cell containing a solution of $LiClO_4$ at specified concentration (6.25, 12.5, 25.0, 50.0, and 100.0 x 10^{-4} M) and temperature (298, 303, 308, 313, 318, 323, and 333K). The conductivity was calculated by:

$$\sigma_s = \sigma \cdot (L/A)$$

where,
σ = conductance measured;
L = distance between electrodes (0.71 cm);
A = electrode area (1.06 cm^2).

Thermal Measurements

DSC measurements were carried out using a SHIMADZU DSC 50 Calorimeter. Experiments were conducted at temperature range of – 173 to 453K and scanning rate of 10K/min. Sample amount of 5 mg was used. The T_g value of the materials was obtained from the second run DSC curves. The thermal stability of the samples was investigated using a SHIMADZU TG 50 instrument at scanning rate of 20K/min. Sample amount of 5 mg was used.

Results and Discussion

Characterization of LDPE/P4VP samples

The FTIR spectra of LDPE films, after *in situ* sorption and thermal polymerization of 4VP, showed bands at 1610 cm^{-1} (υ, C=C of pyridine ring), at 840 cm^{-1} (δ, CH of pyridine ring) and absence of band at 940 cm^{-1} (δ, CH vinyl) which confirmed the presence of P4VP into LDPE matrix.
The characteristics of LDPE/P4VP samples used are described in Table 1.

Conductivity Measurements

The conductivity of different concentrations of $LiClO_4$ solution (0.625 to 10mM) varied from 1.29 x 10^{-3} to 19.17 x 10^{-3} $S.cm^{-1}$.
The conductivity of H_2O used for preparation of $HClO_4$ and $LiClO_4$ solutions was of 1.67 x 10^{-6} $S.cm^{-1}$.

Table 1. Characteristics of LDPE/P4VP materials

Sample (No.)	Mass Increase (%)	Reaction Time (h)
A_1	1.4	1.0
A_2	14.3	2.0
A_3	28.4	4.0
A_4	30.5	6.0
A_5	31.7	8.0

Table 2 shows the conductivity of swollen LDPE/P4VP films measured for specific concentration of electrolyte solution ($LiClO_4$) at 298K. The conductivity depended on $LiClO_4$ concentration increasing from 2.0 x 10^{-6} S.cm^{-1} to 1.213 x 10^{-3} S.cm^{-1}.

The effect of temperature on the conductivity of samples is shown in Table 3. The conductivity increased from 7.0 x 10^{-6} S.cm^{-1} (S_1) to 2.66 x 10^{-3} S.cm^{-1} (S_5) for temperature range of 303 to 333K. Sample S_1 (mass increase of 1.4%) showed, as an exception, a constant value of conductivity (7.0 x 10^{-6} S.cm^{-1}) for all temperatures studied, probably due to its low capacity in promoting ion exchange.

Table 2. Conductivity of LDPE/P4VP samples at 298K.

$LiClO_4$ Concentration (10^{-4}M)	6.25	12.5	25.0	50.0	100.0
Sample(No.)	Conductivity (10^{-6} S. cm^{-1})				
S_1	2	3	4	5	7
S_2	16	17	18	20	21
S_3	267	342	490	729	1187
S_4	260	334	472	714	1168
S_5	279	344	486	741	1213

Table 3. Conductivity of LDPE/P4VP samples at different temperature in 10mM $LiClO_4$ solution.

Temperature (K)		303	308	313	318	323	333
Sample (No.)	Mass increase (%)	Conductivity (10^{-6} S. cm^{-1})					
S_1	1.4	7	7	7	7	7	7
S_2	14.3	23	27	32	38	46	62
S_3	28.7	1254	1380	1546	1773	2034	2620
S_4	30.9	1220	1320	1494	1700	1961	2594
S_5	31.7	1260	1386	1560	1787	2060	2660

The Arrhenius modified ($\ln(\sigma \times T)$ versus T^{-1}) and VTF [$\ln(\sigma)$ versus $1 / (T - T_g + T_o)$] plots for conductivities of LDPE/P4VP membranes was obtained (Figs.1 and 2).The best fit was found for Arrhenius modified equation (linear regression coefficients of 0.999), Fig.1. The VTF plot showed lower linear regression coefficients (0.99), Fig.2. A deviation from linearity for measurements of all samples at room temperature was observed.

Thermal Analysis

The glass temperatures obtained by DSC curves are shown in Table 4. T_g values in the range of 214 to 240 were found for all the samples except sample

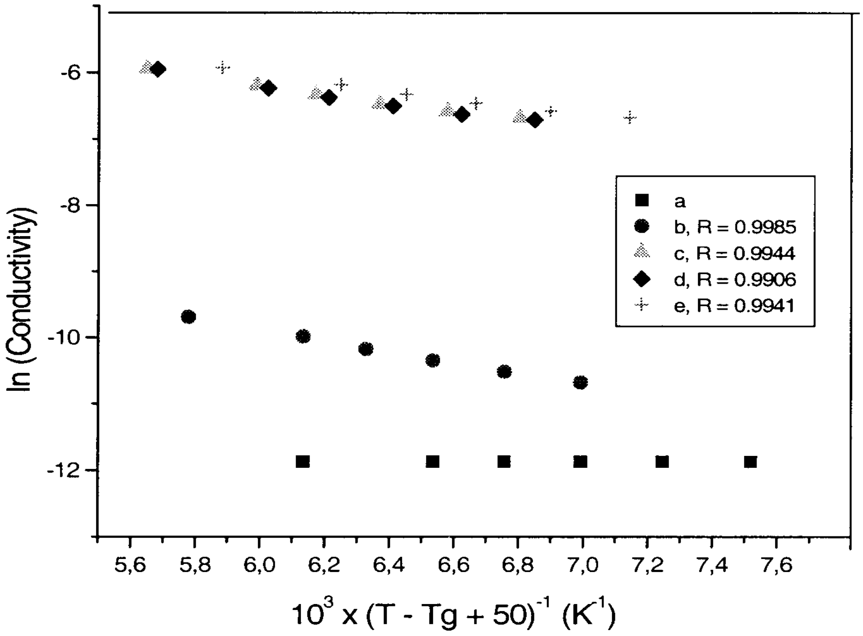

Fig.1 ln(conductivity x T) versus T^{-1}. Mass increase: a) 1.4%;b) 14.3%;c) 28.7%; d) 30.9%; e) 31.7%

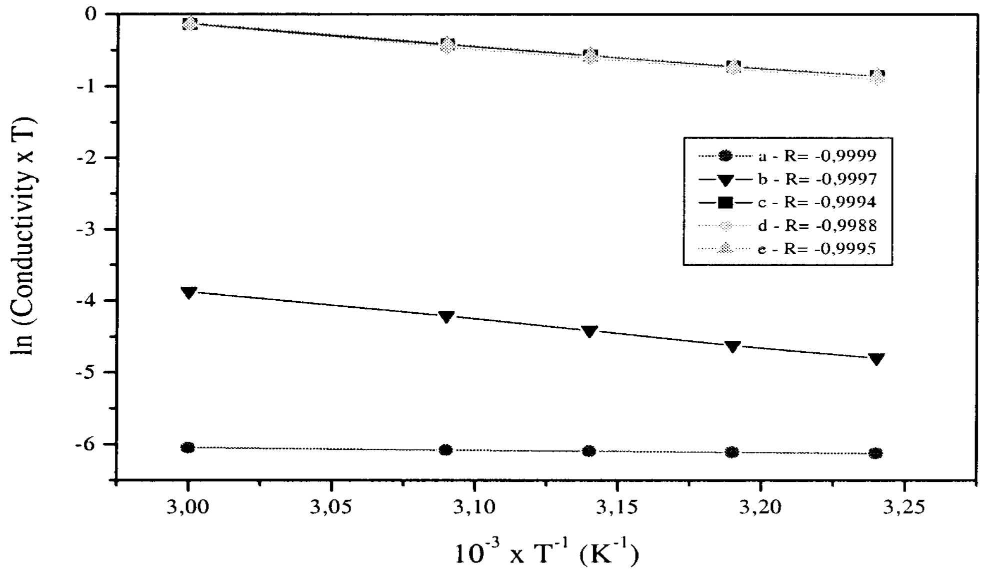

Fig.2 ln(conductivity)versus $10^3 x(T-Tg+50)^{-1}$. Mass increase: a) 1.4 %; b) 14.3%; c) 28.7%; d) 30.9%; e) 31.7 %.

S_1 (mass increase of 1.4 %) that had shown broad transitions of difficult identification. Close T_g values had been found for samples S_2, S_3, S_4 (207, 210 and 213K) which is an indication of absence of clusters structures after ion exchange. However, sample S_5 (mass increases of 31.7%) had shown comparatively, higher T_g value(240K) that could be an indication of cluster formation. A single T_g value reflects a possible absence of micro domains.
Thermo gravimetrics data are shown in Table 4. Pure LDPE showed one decomposition step starting at 743K and finishing at 804K. LDPE/P4VP sample containing low amount of P4VP (S_1) showed degradation curve similar to that of pure LDPE. The remaining samples showed similar curves with two degradation steps. The first step, initiating at 645-654K and finishing at 667-701K, was identified as P4VP degradation chains and the second, starting at 711-743K and ending at 783-796K, as due to LDPE chains degradation (8).

Conclusions

The studies reveal potential utilization of LDPE/P4PV materials, thermally synthesized, as LDPE electrolyte membranes based on an acid-base polymer in the host matrix. The swollen material is a polymer blend in which one of the components (P4VP) is an acid-base polymer entangled in LDPE chains amorphous domains (5,7). The swollen LDPE-P4VP films showed significant conductivity due mainly to ionic motion in solvent-rich regions. The blends function as electrolytes in which the conductivity depends on the P4VP mass increment in LDPE host matrix.
The conductivity dependence with the temperature of LDPE-P4VP samples indicates an activated process. The Arrhenius modified equation provides the best representation for the data of P4VP mass increments studied (< 32%). Higher mass increment materials (56, 82 and 137 %) showed micro phase domains and no significant increment on the conductivity (8). This could be related to relationships between multiphase behavior and transport properties affecting directly the conductivity. The T_g values close to that of LDPE suggest a correlation between ions conductive mode and chain motion of P4VP into the matrix.
Finally, the blends studied (P4VP) mass increment (< 32 %) possesses enough thermal stability for use as an electrolyte membrane.

Acknowledgements

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