OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 2, No. 7, July 2008, p. 442 – 445

FT - IR analysis on polyimide selective membranes

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In this work is reported a FT - IR analysis performed both on polyimide polymeric matrix and on polyimide selective membranes. Through the FT-IR study done it was shown that the water from the aqueous electrolyte solution acts on polyimide completing its imidization. Also, it was put in evidence that water molecules exists absorbed on the membrane's surface. The result complies with other experimental results previously obtained by performing a.c. impedance analysis and thermal analysis.

(Received June 25, 2008; accepted June 30, 2008)

Keywords: Polyimide polymeric matrix, FT-IR analysis, Imidizing effect of water, Membrane

1. Introduction

In order to use a certain polymer to obtain ion selective membranes for sensitive devices, it has to be chosen those polymeric membranes exhibiting a low glass transition point, T_g. The T_g value of the polymer could be lowered by adding certain plasticizers in the matrix to be considered. The commonly used mixture for obtaining selective membranes contains PVC polymer and orto-nitro octyl phenyl ether (o-NPOE) as plasticizer, but this is not fully compatible with the microdevices' surfaces in such way that the selective PVC membranes are peeling out proving a poor adherence. The efforts to obtain workable and useful selective microdevices supposed an extensive research in finding out the suitable polymeric matrix completely compatible with the microdevices technology. Such polymers are the polyimides. These compounds represent one of the most important classes of heterocyclic aromatic polymers. Polyimides are used in microelectronics, optoelectronics, photoresists, non-linear optical materials, aerospace applications, composites and fiber optics. Polyimides are highly used in the optics and electronics area possibly due to their low dielectric constant and low relative permittivity [1].

Polyimide is a polymer which is synthesized from diamine and acid dianhydride. Precursor of polyimide (polyamic acid) is obtained by reacting diamine and acid dianhydride in liquid. Then, polyimide can be obtained through a dehydration and ring-closure reaction [2]. Generally, as polyimide is poor in solubility to a solvent and difficult to process, it is often obtained by making its precursor, which is polyamic acid, into desired form followed by heating. Polyamic acid decomposes by heat or water, thus, it is not good in storage stability.

Polyimides are characterized by high values of the T_g [3], therefore it is compulsory to add a plasticizer in order to improve the processability of the polyimide. Using the thermal analysis it was possible to study the influence of the nature and proportion of the plasticizers added in polymeric polyimide matrix on the glass transition point [1, 2]. There were also carried out ac impedance investigation on the polyimide matrix and polyimide selective membranes [4]. In completion of these previously done investigations on the polyimide selective membranes behavior, FT-IR study on polyimide membranes is reported. From the analytical point of view, the most useful infrared range is between 4000 and 400 cm^{-1}. Using FT-IR analysis it is possible to measure small variations of the absorption for a pure solvent and of a solution in the same solvent, even if its absorbance in infrared is quite important (water case, for instance).

2. Experimental

In order to compare the results of this study with those previously obtained [1, 2, 4], there were used two polyimide varieties, namely: preimidized polyimide (Aldrich) and synthesized polyimide starting from polyamic acid [6]. The plasticizer used was diethylene glycol dibenzoate – DGD, (Aldrich), and a chemical compound compatible with polyimide. The studied polymeric matrix was obtained by dissolving the polyimide in anhydrous dimethylformamide - DMF (Aldrich) at 110^0C under N_2 purge and continuous stirring and then mixing in DGD as plasticizer. The ratio between polyimide solution (25% in anhydrous DMF) and plasticizer was 2:3. The selective membranes tested contained: an electroactive material, calcium ionophore as N, N, N', N' – tetracyclohexyl – 3 – oxapentadiamine (Fluka), a plasticizer as diethylene glycol dibenzoate (Fluka), a lipophilic agent as potassium tetrakis (p-chlorophenyl) borate (Fluka), and polyimide as polymeric support. The membranes compositions were as stated previously [5]. After obtaining the polyimide matrix the electroactive material and the lipophilic agent were added. Due to the high water intake of polyimide it was necessary that all the handlings of the polyimide solution to be done in a dry gloves box with water content lower than 2 ppm.

After obtaining the membranes, it was possible to use them in lab conditions. The membranes' exposure in aqueous electrolyte solution was done in $CaCl_2$, 10^{-2} mol.l^{-1}, for 48 hours. The water used in the experiments was deionized.

The FT-IR spectra were recorded in mid IR, 4000 – 400 cm^{-1} region on SHIMADZU 8900 equipment by applying KBr pellet techniques (using 6% sample) at 4 cm^{-1} resolution.

3. Results and discussion

Polyimides will hydrolytically degrade [3] if used without plasticizer when soaked in electrolyte solution. This is due to the water molecules' attack on the imide ring when the polyimide will experience a reverse imidization, possibly even a depolymerization. Then the polyimide will revert back to polyamic acid. Chain scissor of polyamic acid results in an acid monomer, which will increase the degradation of polyimide. This is due to its high moisture intake that eventually leads to weakening of epoxy matrix. Therefore, polyimide must be end-capped with a much more hydrolycally stable functioning or to be plasticized with a compatible plasticizer as we performed in our experiments.

Over the entire FT - IR spectra studied were observed few characteristic absorption bands of the existing functions as are presented in Table 1.

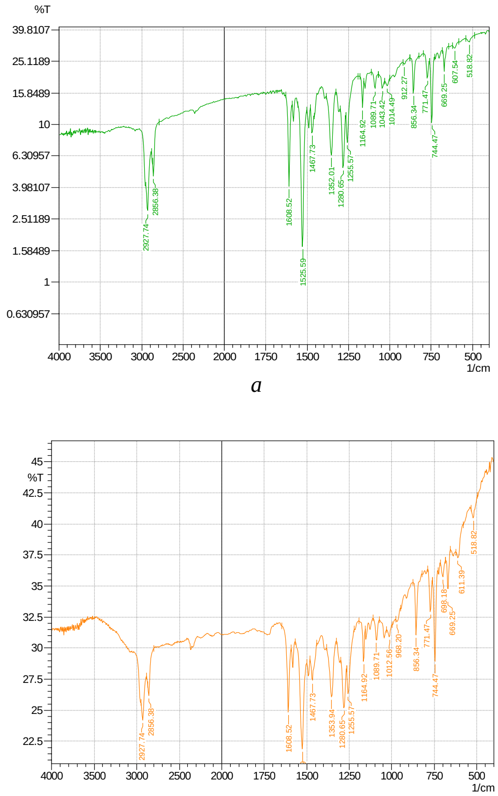
Table 1. Characteristic absorption bands for the studied polyimide membranes

Characteristic group	***Absorption band (cm^{-1})***
Substituted Aryl Group	797
C - O – Ar Symmetrical	1057
C – O - Ar Asymmetrical	1267
$-CH_2$	1427
C = C - Ar	1517
Conjugated Phenyl Group	1600
C = O	1675
N – CO – N	1711
N - H	3085

The imides present in region 3500 – 3200 cm^{-1} a single absorption band. This is shifted towards lower values of the frequencies when it is in condensed state (plasticized), due to the hydrogen bonds which are weaker than the case of the hydroxyl group, due to the lower electro negativity of the nitrogen. This could represent an absorption band due to the combinations of the symmetrical and asymmetrical scissoring vibrations of the N – H bond which could appear due to the π bond of the polyimide.

In Fig. 1 (a, b), the FT-IR spectra recorded for two plasticized polyimide varieties, which were used to obtain ion selective membranes, are presented. The FT-IR spectra of the plasticized membranes showed the presence of a strong / medium absorption band in the region 1650 - 1590 cm^{-1}, which is characteristic for scissor vibration of $-NH_2$, while the valence vibrations of $-NH_2$ are put in evidence by multiple absorption bands of medium or strong intensity, in the region 850 - 750 cm^{-1}. Absorption bands of multiple combinations within the range 2800 - 2000 cm^{-1} are present, and in the region between 1600 - 1400 cm^{-1} appears an absorption band due to the stretching vibrations of the N-H bond. A medium intensity peak recorded at 741 cm^{-1} could be assigned to the C=O bending vibration within the aromatic imide.

The other absorption peaks observed could be assigned to the vibrations of the benzene nucleus and for the structure of the 1, 4 disubstituted benzene.



a

b

Fig. 1. FT-IR analysis for membranes obtained from: a. commercial available polyimide; b. synthesized polyimide.

In our previous work, differential scanning calorimetry (DSC) and thermal analysis (TG) for polyimide precursor (polyamic acid) [6] and polyimide membranes [2, 5] were performed. From the change in latent heat and heat capacity over a temperature range it was possible to determine the glass transition points, melting temperatures and crosslinking temperatures – related to the complete imidization of the polyimidic precursor [6]. The thermal analysis performed showed that the polyamic acid loses water, CO and CO_2 within a temperature range from 25^{0}C to 497^{0}C through subsequent decomposition reactions. The change of the polyamic acid into polyimide through thermal treatment could be also put in evidence by help of FT – IR analysis following the changes occurred in the compounds spectra. Some of the characteristic bands of the polyamic acid, the precursor of polyimide, are presented in Table 2.

Table 2. Characteristic absorption bands for the polyamic acid.

Characteristic group	***Absorption band (cm^{-1})***
Vibrations of the aromatic ring	1491
Bending vibration of N – H bond	1620
Stretching vibration of Amidic bond	1685
Stretching vibration of C - H bond	3100
Stretching vibration of N – H bond	3328

The FT-IR data showed that the imidization by thermal cyclodehydration of the polyamic acid took place completely, as the absorption due to the bond of amidic type are under the detection limit or only a very weak peak is present (at about 2850 – 3100 cm^{-1}, 1655 cm^{-1} and 1540 cm^{-1}), while the absorption due to the imidic bonds are strongly represented.

The thermally treated polyimidic acid film presents the characteristics of the imides structure. There was significant evidence shown in the spectrum that the imidization occurred, the main signals recorded being assigned as follows: at 1606 cm^{-1} the characteristic band for the asymmetrical stretching of vibration for the carbonyl groups; at 1525 cm^{-1} signal for symmetrical stretching of C=O in aromatic imide; at 1353 cm^{-1} the spectral band of the vibrations for the stretching of the C – N bond in aromatic imide, and at 744 cm^{-1} appears the spectral band corresponding to the bending of the imides ring in aromatic imide.

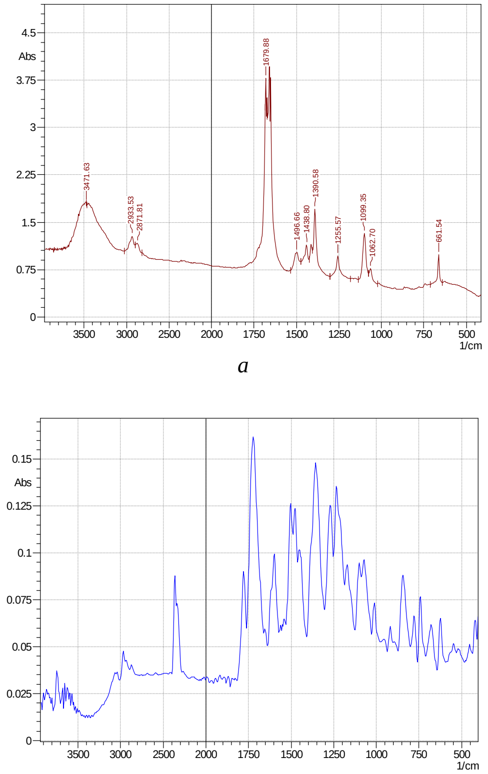
It is also noticed the absence of the absorption band characteristic for the amidic group at 1650 cm^{-1}. Only the presence of a low intensity signal at 1467 cm^{-1} could be assigned to a rest of untransformed polyamic acid in polyimide by the thermal treatment. The carbon triple bond peak at 2310cm^{-1} slowly increased in intensity for the thermally cured precursor of polyimide.

The band from 1608 cm^{-1} presents a reduced intensity when compared with the characteristic band for the symmetrical and unsymmetrical stretching vibrations specific for polyimide from 1726 cm^{-1} and 1780 cm^{-1} which are shifted towards lower values of the wave number due to the condensed state of the polymer as previously mentioned.

It was also studied the spectrum of a polyimide solution obtained under nitrogen and exposed to subsequent UV radiation, in order to put in evidence a possible change of the polymeric solution structure under the UV radiations action.

It could be noticed a higher imidization degree of the polymeric solutions exposed to the UV radiations, the characteristic absorption bands of imides – at 1679 cm^{-1} and 1390 cm^{-1}, being much stronger.

This investigation was performed because the polyimide is commonly used as photoresist in the integrated circuits technology. Therefore, it is of high interest to follow up the change occurring during UV irradiation, as there is the possibility to cast the selective membrane over the microdevice's dielectrical gate from the early stage of the circuit generation [5].



a

b

Fig. 2. FT-IR analysis for: a. "dry" polyimide membrane; b. conditioned polyimide membrane.

In order to study the water's influence on the selective membranes, the FT-IR investigations were performed both on "dry" membranes and on the conditioned (for 48 h) membrane using aqueous solutions of electrolyte. The spectra recorded for the selective membranes considered are presented in figure 2 (a, b).

Comparing the spectra obtained for "dry" membranes and for the conditioned membranes, it was observed that the water acts on the polyimide completing its imidization. As it is shown in figure 2.b., after the membrane's exposure in aqueous solution, in the range 3500 - 3200 cm^{-1} appear the absorption band characteristic to imides. However, the signal from 2200 – 2300 cm^{-1} specific for the carbon triple bond absorption which appears following the crosslinking reaction is almost under detection limit for the conditioned membranes.

As consequence of the polymeric matrix imidization, the combined band from about 2500 cm^{-1}, is shifted towards 3000 cm^{-1} due to a weak hydrogen bond, the polyimide being imidized within a higher proportion. Also, there occurs an exchange in the intensities ratio of the absorption bands in the region 1600 - 1800 cm^{-1}, the specific absorption band for imides from 1720 cm^{-1} being shifted to 1679cm^{-1}. There were several imide peaks that showed the specific bonding, especially at about 1250 – 1400 cm^{-1} characteristic for C-N bonds. The presence of this bond shows that there was a successful imidization, finally an amorphous material resulted.

The calcium-selective polyimide membranes soaked in calcium chloride solution displayed well-resolved bulk impedance semicircles [1]. The impedance spectra of the polyimide membranes were analyzed supposing that within the used frequency range (10^{-5} – 10^{-1} Hz), the selective polyimide membrane behaves as a parallel circuit formed by a capacitance and a resistance [1, 4]. The experimental data showed that the bulk resistance decreased with the membrane conditioning time. This suggests that the energy for transferring calcium ions across the polymer membrane decreased with the increasing conditioning time.

The crystalline morphology of polyimides is important because the necessary properties of the polymer to be used as matrix for selective membranes are directly influenced by the morphology. As Lincon *et al.* [3] suggested there are two structural parameters affecting dramatically membrane's permeation, namely the glass transition temperature (T_g) and the crystallinity. Since transport proceeds mainly via amorphous regions, it is very important to know the crystallinity degree in the polymer. As mentioned before, the FT-IR spectrum of the conditioned membrane put in evidence the formation of an amorphous material. Thus, both analyses performed: the previously done a.c. impedance analysis [1, 4] and FT-IR analysis proved that the polyimide membrane conditioned in an electrolyte solution leads to a functional selective polymeric membrane across which is possible the ions' transfer.

The previously reported data on the polyimide density [6] obtained by help of a gradient column using a mixture of hexanol and tetra chloromethane allowed the calculation of the polymer packing coefficient which was found to be equal by 0.68. This result signifies that 32% out of the polyimide matrix is free volume. Thus, significant water volume could be accommodated within the polymeric matrix. Also, the thermogravimetric data [6] put in evidence the existence of an important quantity of water which was lost in two different decomposition stages between 25^0C and 150^0C. These results are sustained by the FT-IR spectra obtained for conditioned polyimide membranes where the -OH characteristics bands (hydrogen bond) in the 3400 cm^{-1} region were observed, overlapping with those of imides.

4. Conclusions

The performed FT-IR analysis sustained the previously results of the polyamic acid imidization through thermal treatment.

Harmonizing the results of the FT-IR analysis with other experimental data as: impedance analysis [4] and thermal analysis [1, 5, 6] it is possible to state that water completes the imidization of the polyimide polymeric matrix, providing an amorphous material suitable for various ions' transport. However, the polymeric films keep the suitable flexibility for selective membranes due to the presence of the plasticizer. The value of the polymer packing coefficient and the thermal analysis which showed that water molecules are absorbed on the membrane's surface in a large quantity, are also sustained by the FT-IR analysis here performed.

A further scanning electronic microscopy study on the selective polyimide membranes associated with a ternary phase diagram could provide an explanation of the membrane's behavior in electrolyte solutions and also will help in choosing the most suitable composition for certain analyte to be determined.

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