



# Thin films of polymerized acetylene by RF discharge and its benzene absorption ability

A. Arias-Durán<sup>a,b</sup>, L. Giuliani<sup>b</sup>, N.B. D' Accorso<sup>c</sup>, D. Grondona<sup>b</sup>, S. Goyanes<sup>a,\*</sup>

<sup>a</sup> LP&MC, Departamento de Física, FCEyN – UBA, IFIBA, CONICET Ciudad Universitaria 1428, Ciudad Autónoma de Buenos Aires, Argentina

<sup>b</sup> INFIP, CONICET, Departamento de Física, FCEyN – UBA, Ciudad Universitaria 1428, Ciudad Autónoma de Buenos Aires, Argentina

<sup>c</sup> CIHIDECAR-CONICET, Departamento de Química Orgánica, FCEyN – UBA, Ciudad Universitaria 1428, Ciudad Autónoma de Buenos Aires, Argentina

## ARTICLE INFO

### Article history:

Received 19 September 2012

Accepted in revised form 21 November 2012

Available online 29 November 2012

### Keywords:

RF plasma

Polymerization

Acetylene

Benzene absorption

## ABSTRACT

Thin films of polymerized acetylene have been deposited by Plasma Enhanced Chemical Vapor Deposition with a capacitively coupled RF discharge of acetylene. From the results of elemental analysis, FTIR, <sup>1</sup>H-NMR and electrical conductivity, a highly branched chemical structure for the polymeric film is proposed. The morphology of the film surface, as well as its thickness was determined by scanning electron microscopy. The optical constants of the film, refractive index and optical band gap energy were obtained by the UV–vis transmittance spectrum using different models from the literature. The films presented a moderate degree of hydrophobicity and showed a high capacity to absorb and retain benzene after drying at room temperature during 24 h. This result shows the potential of the obtained polymer to be used in filler of filters employed for the treatment of industrial effluents.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Plasma assisted polymerization is defined as the formation of a polymeric material under the influence of plasma. This technique is used for the production of new materials and for the modification of polymeric surfaces. The polymers produced by plasma polymerization do not show a regularly repeated structural unit; they form crosslinked structures with properties that differ from that of linear polymers synthesized by chemical methods. These plasma polymers can be of great interest in fields of technique such as electronics, health and optics applications and can be used in the development of new technologies. The capacitively coupled radio frequency discharge is an easy technique to produce plasma polymer films, this method consists in a one step process compared to the conventional polymerization and the films obtained are highly dense and show a very good adhesion on a great variety of substrates [1]. Plasma polymerization has been studied extensively since the 1950s. Carbonaceous films were prepared by König [2] and colleagues with a glow discharge in benzene where they fabricated a hard polymer (C:H) and materials similar to amorphous hydrogenated carbons (a-C:H) [3,4]. Jesch et al. [5] reported an infrared spectroscopic structural data of a number of polymers produced by a glow discharge applying an electric field to the vapor of different organic compounds using a parallel-plate electrode arrangement powered at 250 V ac at 20 kHz. The infrared (IR) absorption spectra show that the obtained polymers contain many identifiable unsaturations in the form of both olefinic bonds and free valences.

In the particular case of the acetylene polymer obtained by different plasma techniques [4,6–9] studies on surface properties have been reported such as hydrophobicity, mechanical and electronic properties. Moreover, the substituted polyacetylenes proved to be humidity sensitive materials [10,11] but there are very few reports on the application of plasma polymerized acetylene films in humidity or chemical sensors. Chen et al. [12] studied the ethanol vapor sensitivity of plasma polymerized film from acetylene and nitrogen containing mixtures by performing a chemical characterization of the films.

In this work, films were prepared by plasma polymerized acetylene using a capacitively coupled radio frequency discharge. The polymer molecular structure was inferred by nuclear magnetic resonance techniques, elemental analysis and infrared spectroscopic data. The electrical and thermal properties were evaluated and the obtained results are those expected from the chemical proposed structure. Besides, optical properties and adhesion of the polymer films to different substrates were studied. Moreover, the capacity of this polymer to capture benzene was demonstrated by UV–vis spectroscopic studies.

## 2. Experimental

### 2.1. Plasma polymerization

The reactor employed for the polymerization consisted in a vacuum chamber made of stainless steel pumped to a base pressure of 10<sup>−6</sup> mbar. The electrodes were flat circular plates made of stainless steel with diameters of 80 mm separated from each other a distance of 10 mm. One of the electrodes was connected to the RF power supply (13.56 MHz, 600 W) through a matching unit and the other electrode

\* Corresponding author. Fax: +54 11 4576 3357.

E-mail address: [goyanes@df.uba.ar](mailto:goyanes@df.uba.ar) (S. Goyanes).

was grounded. The discharge duration was 10 min with an output RF power applied of 50 W. Films were deposited on silicon, quartz and glass substrates placed on the grounded electrode. The temperature of the substrate was measured with a thermocouple. The temperature of the substrate increased about 20 °C during the discharge. The reactor was operated at room temperature with acetylene gas of commercial grade. The gas flow rate was 20 sccm and the pressure was held constant at 0.12 mbar. The reactor is sketched in Fig. 1.

## 2.2. Characterization

The surface morphology of acetylene polymerized thin films was characterized by Field Emission Scanning Electron Microscopy (FE-SEM Zeiss LEO 982 GEMINI). From FE-SEM images of film cross-sections, the film thickness was estimated.

A “Scotch tape test” was used to qualitatively determine the adhesion strength of the polymer films to the substrates (quartz, glass or silicon). A Scotch tape was firmly pressed to the surface of the plasma polymer film and then pulled away. The scotch tape and the substrate with the polymer film deposited were examined in an optical microscope to determine whether material was detached or if the film was peeled off the substrate.

<sup>1</sup>H-NMR spectrum was recorded on a Bruker AC-200 spectrometer operating at 200 MHz, using CDCl<sub>3</sub> as solvent. The infrared spectrum was recorded on a Nicolet 510P spectrophotometer using the Attenuated Total Reflectance (ATR) mode. Elemental analysis was performed on an Exeter Analytical CE-440 elemental analyzer to determine carbon and hydrogen percentage. A four-point probe set up, homemade built, and a Keithley 199 System DMM/Scanner multimeter were used to measure conductivity of the films.

Film UV–vis spectrum was performed with a Shimadzu UV-1800 spectrophotometer in transmittance mode. From this spectrum, the refractive index, *n* and the film thickness *d* were calculated by the Goodman method [13]. Besides, the band gap energy was calculated from the Tauc method [14].

Thermogravimetric analysis was used to study the thermal decomposition of the polymer film. The device employed was a DTG60 Shimadzu. The temperature range was 30–700 °C at a heating rate of 10 °C/min with a nitrogen flux of 30 mL/min.

The chemical structure inferred from previous studies suggested the possibility that this material may experience strong swelling when it is immersed in a benzene-type solvent. If this were true the material should have some degree of hydrophobicity. To evaluate this, contact angle measurements were performed using a distilled water drop (Goniometer Type G-1, Erma Optical Works Co. LTD). The drop method was conducted at ambient environment and each drop was fixed at 0.9 µL. Contact angle was taken as an average of fifteen measurements for each sample.

## 2.3. Benzene absorption ability

The ability to absorb benzene was evaluated using acetylene polymer powder obtained by scrapping the polymer film. This powder was immersed in benzene (20 mL) for 24 h under stirring during the first 4 h. After this time, the polymer powder was filtered and dried at room temperature and atmospheric pressure during 12 and 24 h (samples (a) and (b), respectively). The effect of benzene absorption was determined from the results of absorption in the UV–vis spectrophotometer. This study was conducted on the following solutions: (1) 12 mL of benzene in 10 mL HPLC grade tetrahydrofuran (THF), (2) 0.95 mg of the acetylene polymer in 10 mL of THF, (3) 0.95 mg of sample (a) in

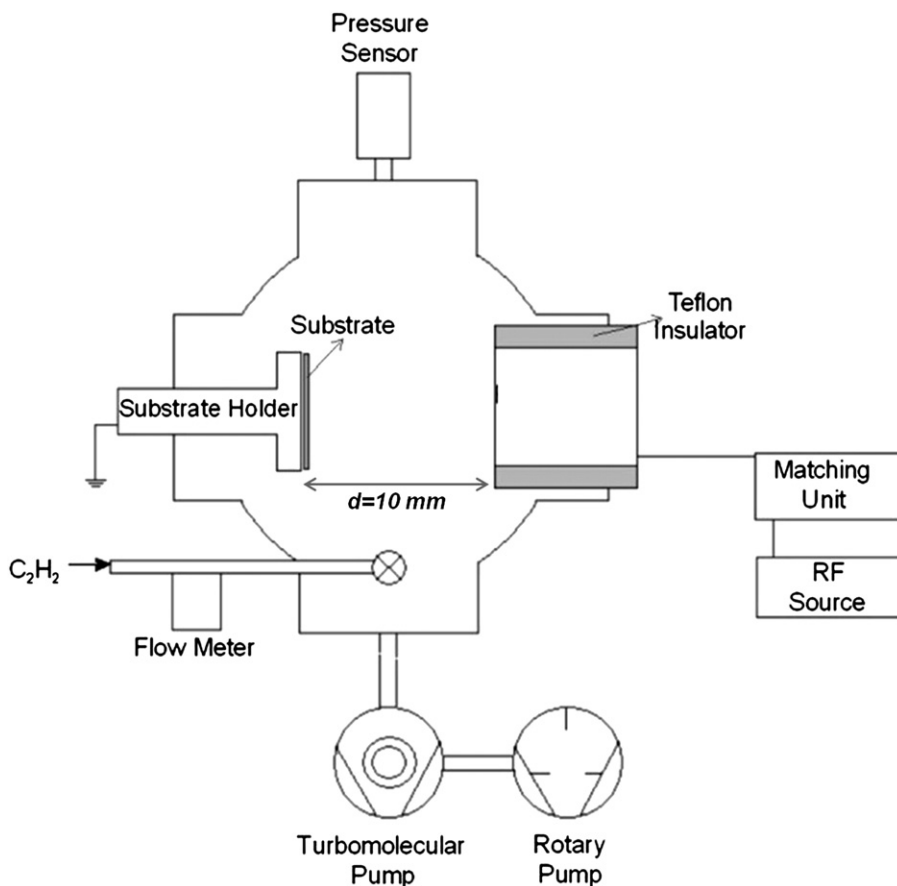


Fig. 1. Experimental RF plasma reactor employed for the polymerization.

10 mL of THF and (4) 0.95 mg of sample (b) in 10 mL of THF. The two latter samples saturated the equipment because the absorbance of the material was higher than the maximum detectable, whereby, in these two cases the spectra were obtained on samples with dilution four times greater than that used for the polymer prior to its exposure to benzene (0.95 mg of sample (a) or (b) in 40 mL of THF).

### 3. Results and discussion

#### 3.1. Surface morphology

Fig. 2(a) shows an FE-SEM microscopy of the acetylene polymer film. As can be seen, the surface of the plasma polymer acetylene has a number of agglomerates of clusters bonded together, with average diameters between 50 and 70 nm, estimated by the image processing software ImageJ. It is possible that the surface morphology presented by the film is related to the agglomeration of carbonaceous nanoparticles formed by nucleation of negative radicals ions of CH and others electrically charged species, according to the model proposed by Eva Kovacevic et al. [21] which describes the formation of this type of clusters in RF discharges in an atmosphere of acetylene.

Fig. 2b shows a FE-SEM micrograph along the cross section of the polymer acetylene film on a Si substrate. The equipment has its barrel at 90° of the surface and is calibrated to determine the thickness from micrographs. From Fig. 5b the film thickness can be estimated as  $(625 \pm 5)$  nm.

From the “Scotch tape test” it is possible to conclude that the polymer-film has the weakest adhesion to the glass substrate; large areas of the acetylene polymers were removed from the glass surface. The adhesion of the film to the Si substrate was better than to the glass but it was not good because same areas of the film were peeled off the substrate. The quartz substrate exhibits the strongest adhesion, no material was observed on the Scotch tape.

#### 3.2. Polymer chemical structure

Fig. 3 shows the spectrum of proton nuclear magnetic resonance,  $^1\text{H-NMR}$ , of RF plasma polymerized acetylene dissolved in deuterated chloroform (highest signal). The spectrum shows signals around 6 ppm corresponding to vinyl protons ( $=\text{CH}$ ), which made it possible to infer the polymerization of acetylene. Moreover there are signals that can be attributed to unprotected aliphatic carbons and up field signals that indicate more protected protons. These last signals can be assigned to the presence of some aliphatic protons, allowing the formation of branches, generating thus a crosslinked material. That is, in the formed polymer four different proton types, whose relations obtained from the integration areas are 1:3:2:20 for a total of 26 protons, can be distinguished.

An initial elemental chemical analysis shows that the obtained material not only is composed primarily of carbon and hydrogen as expected, but also has a percentage of oxygen and a small percentage of nitrogen. Using a fixed microanalysis and neglecting the minimum percentage of nitrogen, the following relationship is obtained for percentages of carbon, hydrogen and oxygen respectively, at  $\%C = 76.09\%$ ,  $\%H = 6$  and  $\%O = 17.03$ . From these results a minimum formula  $\text{C}_{12}\text{H}_{13}\text{O}_2$  is suggested, however, considering the NMR spectrum, a corrected formulae corresponding to the 26 protons observed in the NMR spectrum was proposed, having then  $\text{C}_{24}\text{H}_{26}\text{O}_4$ . This formula has twelve unsaturations corresponding to the presence of double bonds or non-aromatic cyclic in the structure. This last statement is a consequence of the previous NMR analysis due to the absence of signals at lower fields ( $\delta \approx 7$  ppm) that based on NMR can indicate that there are six  $\text{C}=\text{C}$ , a  $\text{CH}_2$  checked around 3.55 ppm, and ten other unprotected  $\text{CH}_2$  less about 1.66 ppm, leaving a carbon and four olefinic protons (1 to 5.80 ppm and 3 to 4.26 ppm). Based on these results, a schematic of the chemical structure of the polymer formed by the polymerization of acetylene plasma could be that shown in Fig. 4. As shown in the diagram there is a high degree of conjugation but this is not complete, i.e. there is a discontinuity in the conjugation by which the polymer would not be a good electrical conductor as the acetylene polymer produced by chemical synthesis (characterized by its linear conjugation). The presence of oxygen is justified because the acetylene used is of commercial grade.

To verify that the plasma polymerized acetylene does not possess a complete conjugation, electrical conductivity was measured using the 4-point technique. The resistance value exceeded the maximum value measurable by the equipment employed, 12 M $\Omega$ , indicating that the polymer is an insulator and endorsing the idea of the low periodicity in the estimated conjugation in previous studies. Finally, the structure suggested for the formed polymer also agrees with the results obtained in the study of infrared spectroscopy.

The FTIR spectrum obtained using ATR technique is shown in Fig. 5. The absorption bands around  $3300\text{ cm}^{-1}$  are associated to  $\nu^s\text{-OH}$ . In accordance with the structure proposed in Fig. 3, the hydrogens marked in blue and red justify the shoulders located in  $3012\text{ cm}^{-1}$  and  $3050\text{ cm}^{-1}$  which are associated to carbon with  $\text{H sp}^2$ -hybridization. The band centered at  $2931\text{ cm}^{-1}$  and the shoulders at  $2970\text{ cm}^{-1}$  and  $2869\text{ cm}^{-1}$  are associated to the  $\nu^s\text{Csp}^3\text{-H}$  stretching mode. The band at  $1599\text{ cm}^{-1}$  corresponds to stretching  $\text{Csp}^2=\text{Csp}^2$  while the band located at  $1441\text{ cm}^{-1}$  is associated with  $\text{Csp}^3-\text{Csp}^3$  single bonds, and the band at  $1367\text{ cm}^{-1}$  corresponds to stretching of methylenes. In accordance with the foregoing, the acetylene plasma polymerized film is formed by poly-acetylene in both, cis and trans configurations [15].

The functional groups observed in the FTIR spectrum, as well as the groups forming the entire proposed chemical structure corresponds to

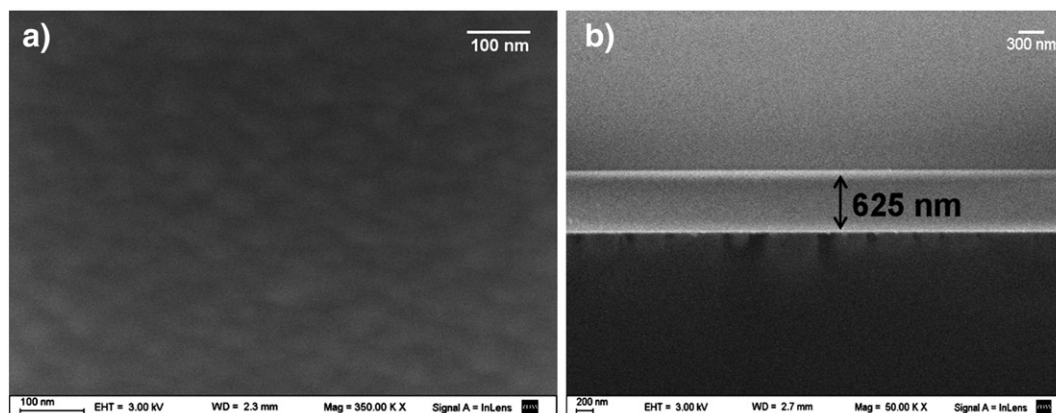


Fig. 2. FE-SEM micrographs of acetylene polymerized thin film on Si substrates. (a) surface film image of 350 KX magnification, (b) cross section image of 50 KX magnification.

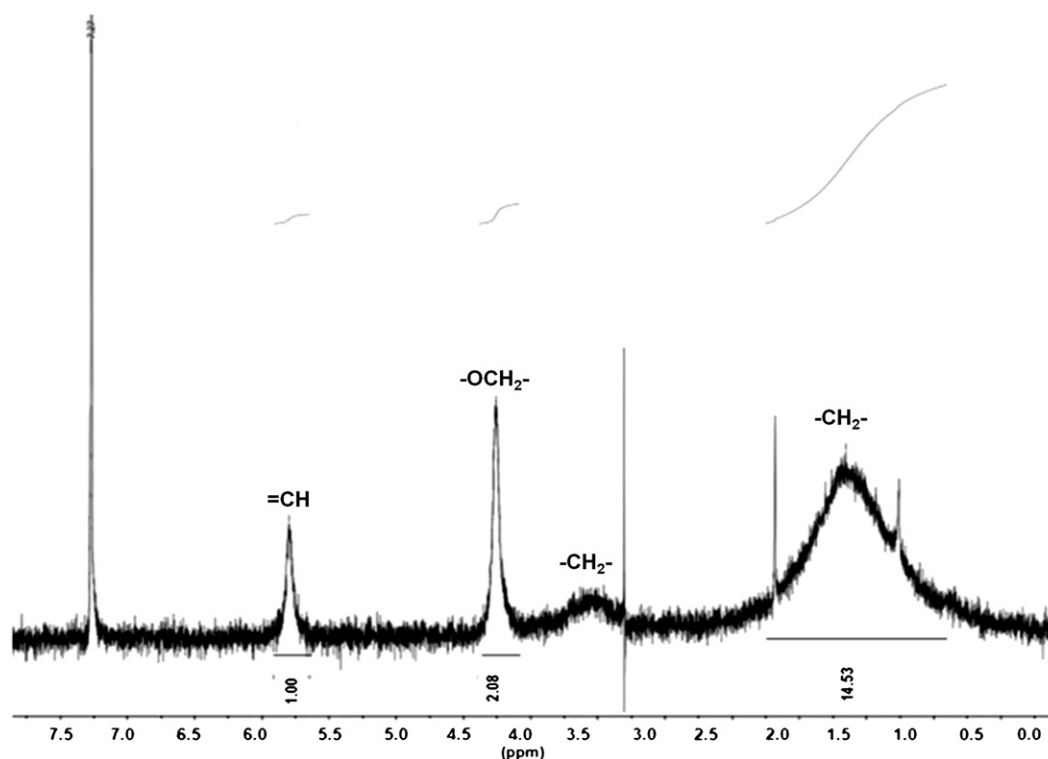


Fig. 3.  $^1\text{H}$ -RMN spectrum performed at 200 MHz using deuterated chloroform as solvent of plasma polymer acetylene.

species found in plasmas of acetylene at low temperatures and powers below 50 W with this type of electrical discharges [16–20].

### 3.3. Thermal degradation

Fig. 6 shows a thermogram of the obtained polymer. The thermal degradation takes place between 300 °C and 500 °C. Note that this wide degradation range is also in accordance with the proposed fact that the obtained polymer is highly branched. Interestingly, at 700 °C a residual mass of the order of 30% remains. It is worth noting that these

results show that this polymer could be used without degradation at temperatures as high as 300 °C.

### 3.4. Optical properties

Fig. 7 shows the UV–vis spectrum of polymerized acetylene film on a quartz substrate. A strong increase in the transmittance above 400 nm can be seen. Also, it can be observed that the spectrum presents an interference pattern produced at the interface substrate–film. The refractive index obtained by the method of Goodman [13] was  $1.7 \pm$

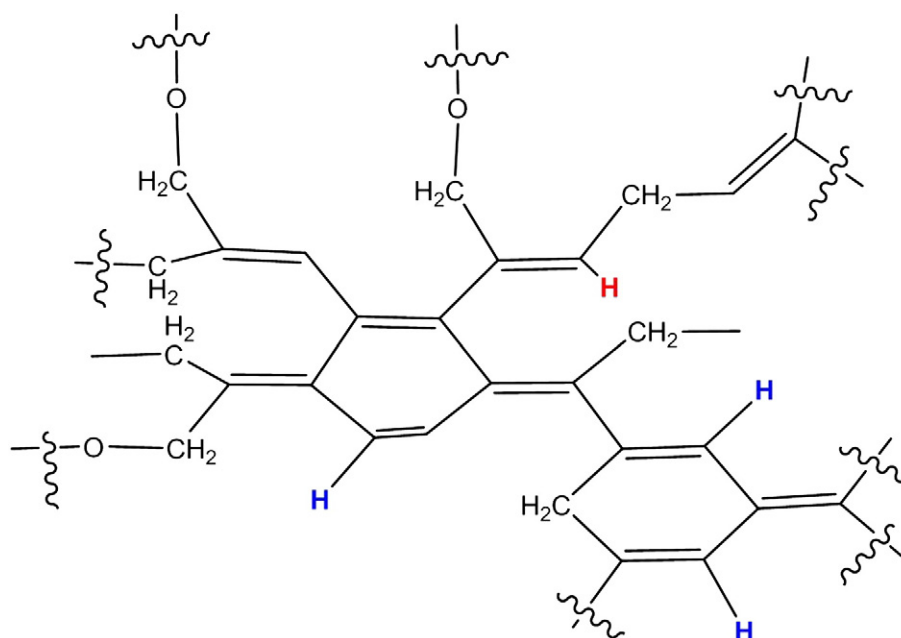


Fig. 4. Molecular structure proposed for the plasma polymer acetylene.

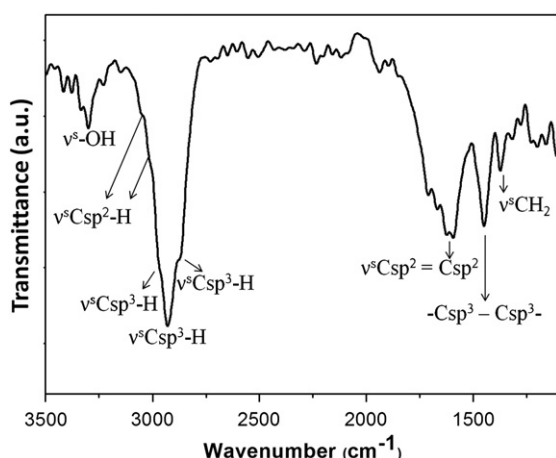


Fig. 5. FTIR spectrum using ATR technique of plasma polymer acetylene on a Si substrate.

0.1 for wavelengths between 680 nm and 980 nm. From an analysis of the interference maxima and minima and taking into account the basic equation for the interference fringes, the films thickness can be calculated as:

$$d = m\lambda/2n. \quad (1)$$

Where  $n$  is the refractive index of the film,  $\lambda$  is the wavelength of the incident light and  $m$  is an integer (semi whole) indicating the order of the interference maximum (minimum). The film thickness calculated from Eq. (1) was  $(580 \pm 50)$  nm, in accordance with the value obtained with the microscope FE SEM in transverse mode.

The optical band gap ( $E_g$ ) was calculated using the Tauc model [14]. It is assumed that the maximum of the valence band and the minimum of the conduction band can be approximated by parabolas described by the following equation:

$$(\alpha E)^{1/2} = \beta(E - E_g) \quad (2)$$

where  $\alpha$  is the absorption coefficient,  $\beta$  is a proportionality constant and  $E$  is the energy of the incident photon. The absorption coefficient can be calculated as:

$$\alpha = -\ln(T)/d \quad (3)$$

where  $T$  is the transmittance showed in the UV–vis spectrum (Fig. 7). In Fig. 8  $(\alpha E)^{1/2}$  was plot against the incident photon energy and the optical band gap was determined from the extrapolation to the

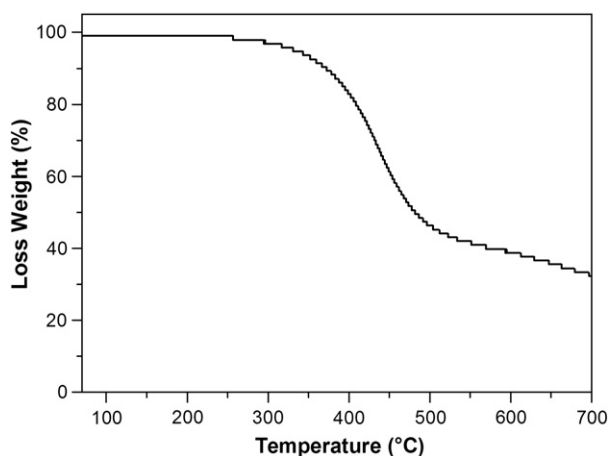


Fig. 6. TGA of plasma polymer acetylene in  $N_2$  atmosphere.

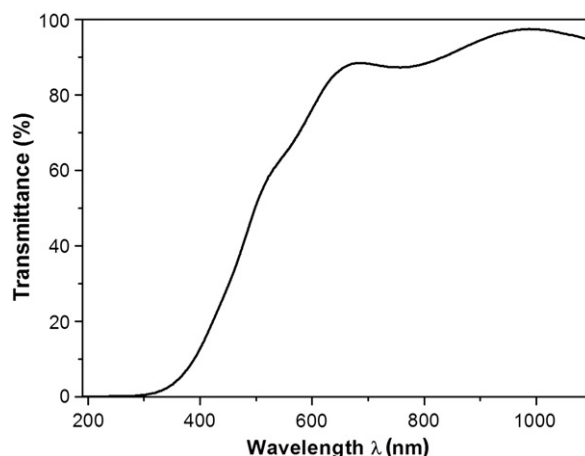


Fig. 7. UV–vis spectrum of acetylene polymerized thin film deposited on a quartz substrate.

abscissa of the linear curve fit between two photon energies corresponding to wavelengths between 330 nm and 460 nm, range in which the absorption of the material occurs. The obtained value was  $E_g = (1.9 \pm 0.1)$  eV, which is approximate to the nominal value of the polyacetylene neutral state [22,23]. This result confirms the insulating nature of our acetylene polymer because of its high degree of crosslinking and low conjugation.

### 3.5. Benzene retention

The chemical structure proposed in Fig. 2 for the obtained polymer suggests that it could interact with aromatic solvents. In particular, it should have some response when exposed to benzene, a highly carcinogenic aromatic solvent. To evaluate this possibility, a study of hydrophobicity was conducted. If the obtained polymer was hydrophobic would be another indication that it could absorb nonpolar solvents such as benzene.

#### 3.5.1. Hydrophobicity

Fig. 9 shows a water drop on the polymer surface. The contact angle measured was  $(66^\circ \pm 1^\circ)$ , which indicates a moderate degree of hydrophobicity. This value guarantees the presence of some surface hydroxyl groups as has been proposed in the scheme of Fig. 3.

#### 3.5.2. Benzene response

Fig. 10 shows the UV–vis absorption spectra of benzene and of the polymer samples obtained prior exposure to benzene and after the

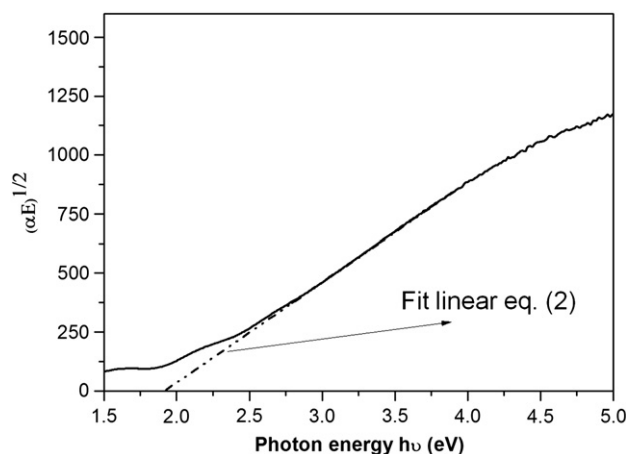


Fig. 8.  $(\alpha E)^{1/2}$  vs incident photon energy  $E$ , for plasma polymer acetylene deposited on a quartz substrate.



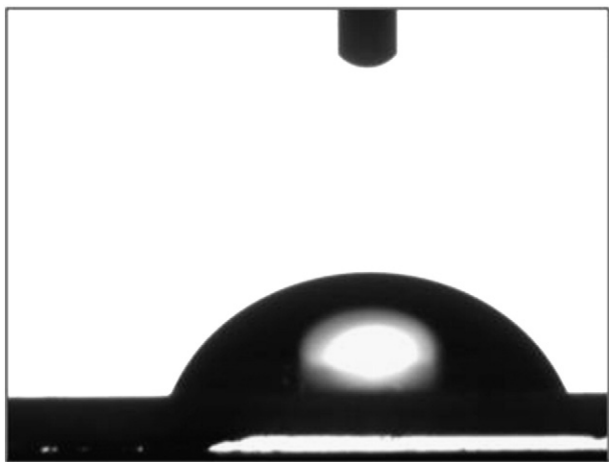


Fig. 9. Photograph of a water droplet on a thin film of acetylene polymerized.

exposure and subsequent drying for 12 h and 24 h. It is important to note that the samples dried for 12 h and 24 h did not show differences in their spectra. These spectra were performed with a dilution four times greater than that used for the polymer prior to its exposure to benzene to prevent the equipment saturation. Therefore, the spectrum of the polymer sample prior to immersion in benzene has a concentration four times higher than the spectrum shown for the polymer sample immersed in benzene and dried.

In Fig. 10 the typical spectrum of benzene with the absorption band corresponding to the transitions  $\pi-\pi^*$  between 227 and 270 nm is shown. The spectrum of the obtained polymer presents a broad band, associated with the transitions  $\pi-\pi^*$ , with an extinction coefficient  $\epsilon = 0.1 \text{ (M}^{-1} \text{ cm}^{-1}\text{)}$  and with an absorption maximum at  $\lambda = 274 \text{ nm}$ . In the spectrum of the sample exposed to benzene and dried 24 h there is an absorption band with an extinction coefficient  $\epsilon = 0.3 \text{ (M}^{-1} \text{ cm}^{-1}\text{)}$  and centered at  $\lambda = 277 \text{ nm}$  with a slight shift respect to the band that presents the polymer before exposure to benzene. This small bathochromic shift, linked to a higher extinction coefficient, allows to infer a cloud  $\pi$  interaction of benzene with the polymer obtained, suggesting that benzene was absorbed by the polymer and it modifies the interaction of  $\pi-\pi^*$  of the polymer. Note that there is no absorption band characteristic of benzene, but the absorption band is centered at a wavelength  $\lambda$  similar to plasma polymer acetylene, this suggest that the trapped benzene is not interacting with itself but modifies this polymer transitions as a result of changes in the network due to its swelling by the presence of benzene.

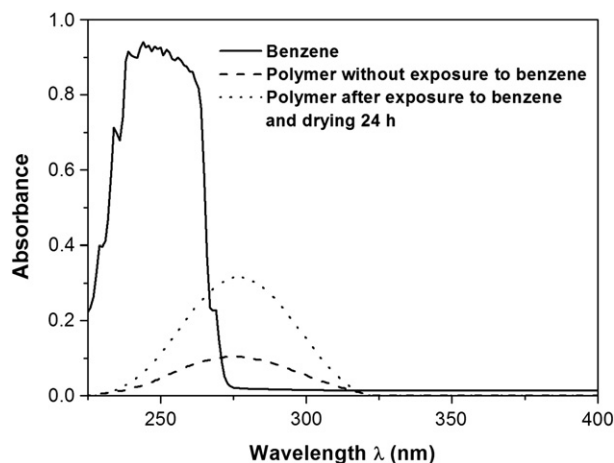


Fig. 10. UV-vis spectra of benzene, plasma polymer acetylene, and plasma polymer acetylene after the exposure and subsequent drying for 12 h and 24 h.

#### 4. Conclusions

The polymerization of acetylene using RF plasma led to a highly branched polymer structure which could be inferred from studies of the combination of  $^1\text{H-NMR}$ , elemental analysis and FTIR. Electrical and thermal characterizations endorsed some responses expected from the chemical structure proposed. The polymer showed a refractive index of  $1.7 \pm 0.1$  and an optical band gap of  $(1.9 \pm 0.1) \text{ eV}$ . Finally, it was demonstrated by UV-vis spectroscopy that the obtained acetylene plasma polymer is capable of interacting with carcinogenic pollutants such as benzene, this plasma acetylene polymer can be used as coating extractors in chemical industries or as filler for filters to decontaminate industrial effluents.

#### Acknowledgments

This work was supported by grants from Universidad de Buenos Aires, UBA (UBACYT Nos.: 20020100100350, 200220100100142), CONICET (2010-2012 PIP 11220090100699, 2009-2011 PIP 112-200801-00064, 2012-2014 PIP 1122011010037 CO), ANPCyT 2007-00291 and INFIP (2010-2012 PIP 11220090100219).

#### References

- [1] F. Shi Frank, Surf. Coat. Technol. 82 (1996) 1.
- [2] H. König, G. Helwig, Z. Phys. 129 (1951) 491.
- [3] J. Goodman, J. Polym. Sci. 44 (1960) 551.
- [4] L.V. Gregor, IBM J. 2 (1968) 140.
- [5] K. Jesch, J.E. Bloor, P.L. Kronick, J. Polym. Sci. 4 (1966) 1487.
- [6] T.S. Liang, K. Akagi, H. Shirakawa, Synth. Met. 101 (1999) 67.
- [7] H. Biederman, D. Slavínská, Surf. Coat. Technol. 125 (2000) 371.
- [8] L. Zajickova, S. Rudakowski, W. Becker, D. Meyer, M. Valtr, K. Wiesemann, Thin Solid Films 425 (2003) 72.
- [9] Heon Kang, Bull. Korean Chem. Soc. 30 (2009) 2589.
- [10] Y. Li, M.J. Yang, Sens. Actuators B 87 (2002) 184.
- [11] Y. Li, Mujie Yang, Synth. Met. 129 (2002) 285.
- [12] Ko-Shao Chena, Ta-Chin Wei, Ming-Shu Li, Hsin-Ming Wu, Tzu-Piao Tang, Chieh-Ying Wang, Yu-Chieh Tu, Radiat. Phys. Chem. 76 (2007) 941.
- [13] Alvin M. Goodman, Appl. Optics 17 (1978) 2729.
- [14] J. Tauc, R. Grigorovici, A. Vancu, Phys. Status Solidi 15 (1966) 627.
- [15] Gwénaëlle Le Dü, Natacha Celini, Faiza Bergaya, Fabienne Poncin-Epaillard, Surf. Coat. Technol. 201 (2007) 5815.
- [16] J. Friedrich, Plasma Process. Polym. 8 (2011) 783.
- [17] A.R. Terje Hansen, Richard van de Sanden, Richard Engeln, Plasma Process. Polym. 8 (2011) 832.
- [18] S. Vizireanu, S.D. Stoica, C. Luculescu, L.C. Nistor, B. Mitu, G. Dinescu, Plasma Sources Sci. Technol. 19 (2010) 034016.
- [19] J. Benediikt, J. Phys. D: Appl. Phys. 43 (2010) 043001.
- [20] E. Valderrama, M. Favre, H. Bhuyan, H.M. Ruiz, E. Wyndham, J. Valenzuela, H. Chuaqui, Surf. Coat. Technol. 204 (2010) 2940.
- [21] Eva Kovacevic, Johannes Berndt, Thomas Strunskus, Laifa Boufendi, J. Appl. Phys. 112 (2012) 013303.
- [22] J. Hegger, Rev. Mod. Phys. 73 (2001) 687.
- [23] V.M. Skorobogatov, I.V. Krivoshei, Russ. Chem. Rev. 57 (1988) 461.