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Conductivity and Activation Energy in Polymers Synthesized by Plasmas of Thiophene

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Abstract. The electric conductivity, activation energy and morphology of polythiophene synthesized by radiofrequency resistive plasmas are studied in this work. The continuous collisions of particles in the plasma induce the polymerization of thiophene but also break some of the monomer molecules producing complex polymers with thiophene rings and aliphatic hydrocarbon segments. These multidirectional chemical reactions are more marked at longer reaction times in which the morphology of the polymers evolved from smooth surfaces, at low exposure time, to spherical particles with diameter in the 300-1000 nm interval. Between both morphologies, some bubbles are formed on the surface. The intrinsic conductivity of plasma polymers of thiophene synthesized in this way varied in the range of 10^{-10} to 10^{-8} S/m; however, the conductivity resulted very sensitive to the water content in the polymers, which produced variations of up to 5 magnitude orders. The activation energy of the intrinsic conductivity was between 0.56 and 1.41 eV, increasing with the reaction time.
Keywords: Plasma, Polymerization, Polythiophene, Conductivity, Activation Energy

Resumen. En este trabajo se estudia la síntesis por plasmas resistivos a radiofrecuencia de politiofeno, su conductividad eléctrica, energía de activación y morfología. Las continuas colisiones de partículas en el plasma inducen la polimerización del tiofeno pero también rompen algunos anillos del monómero produciendo polímeros complejos con anillos de tiofeno y segmentos de hidrocarburos alifáticos. Estas reacciones químicas multidireccionales son más marcadas en tiempos de reacción largos donde la morfología de las películas evoluciona de superficies lisas, a bajos tiempos de reacción, hasta la formación de partículas esféricas con diámetros de 300 a 1000 nm. Entre ambas morfologías, algunas burbujas se forman sobre la superficie. La conductividad intrínseca de los politiofenos sintetizados de esta manera varía en el intervalo de 10^{-10} a 10^{-8} S/m, con conductividad sensible a la humedad de los polímeros, la cual produce variaciones de hasta 5 órdenes de magnitud. La energía de activación relacionada con la conductividad intrínseca se calculó entre 0.56 y 1.41 eV, incrementándose con el tiempo de reacción.
Palabras claves: Polimerización, plasma, politiofeno, conductividad, energía de activación

Introduction

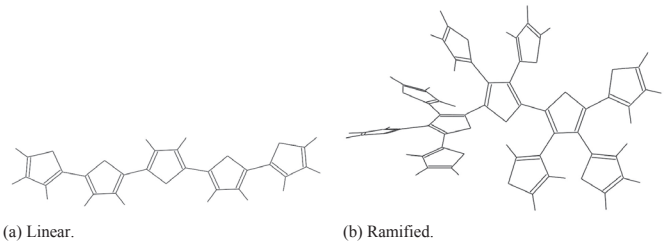
The semiconductor characteristics of polymers play an important role in their electrical and optical potential applications. Polythiophene (PTh) and derivatives have structures with capacity to transport electric charges due to their heteroaromatic electronic distribution. Many experimental and theoretical works have been developed in order to explain the transport of electric charges through the structure of PTh. The most studied polythiophenes have been those resulted from chemical syntheses in liquid-phase. However, the studies about plasma polymerizations of thiophene in gas-phase have left many open questions regarding the electronic structure of polymers that have been subjected to the impact of high-energy particles.

In plasma, the collisions of accelerated electrons and charged particles with the monomer molecules creates radicals and polarized groups, which combine to form complex structures in linear, networked and ramified configurations. High-energy particles can lead to the degradation of the monomers during the polymerizations, but on the opposite, low-energy particles usually produce oligomers instead of polymers. As these structures are formed without initiators, catalysts, solvents or any other agent different from the initial monomer, all the components in the final products are monomer molecules and unsaturated fragments.

From a spatial point of view, each thiophene ring has a planar configuration and may form polymers with rings at different angles; see Fig. 1(a). Linear chains have more probability to align among them forming ordered arrangements, but other structures may produce disordered material; see Fig. 1(b). The final structure can be combinations of those formations as a consequence, mainly, of the energy applied to the polymerization. The relationship between the atomic structure and the final electrical properties of the material make the method of synthesis a critical subject in the polymerization of thiophene.

In chemically synthesized PTh, H. Subramanian theoretically studied some PTh derivatives which could have lower activation energy than the PTh itself [1]. M. Granstrom experimentally studied light emitting diodes using polythiophenes, where the electronic band gap influences the color of the emitted light [2]. On the other hand, J.H. Schon [3] reported that, under certain conditions, derivatives of polythiophene can reach superconductivity. This last work suggests that the electric charges do not have to travel along the polymer chains before passing to another chain. The charges may jump among chains in conductive ordered sections surrounded by amorphous material.

In the case of plasma PTh, there are only a few published works devoted to the study of the synthesis by plasma



(a) Linear. (b) Ramified.

Fig. 1. Representation of PTh structure.

and the electric characteristics. For example, Bhat and Ryan described the thiophene and 2-iodothiophene polymerization by radiofrequency (rf) plasmas respectively [4,5]. In the first work, the polymer resulted with crosslinking and with a low electrical conductivity, between 10^{-15} and 10^{-10} S/cm. In the second work, the polymer was affected by the fragmentation of the precursor molecules, with the consequent loss of sulfur and iodine, because of the increasing discharge power. M.S. Silverstein studied the molecular structure of plasma polymers of thiophene (PPTh) from the point of view of the electrical properties [6]. Yu [7] studied another application of PTh, as protective films against corrosion in microelectronic devices. In the search for transparent and conductive polymer films, L.M.H. Groenewoud [8-10] synthesized and doped derivatives of PPTh.

Results

Thickness of films

The thickness of PPTh films synthesized in this work was measured with a Mitutoyo Micrometer sampling 10 times in different zones of the reactor. The polymers grew as sequential films with different thickness due to small variations in the conditions of synthesis. The formation of films is especially sensitive to variations in the pressure of the system, which is always oscillating around a central value. The pressure of this work was in the range of 10^{-2} Torr.

The individual thickness of some films can be measured in the morphological section and the total thickness is shown in Figure 3 as a function of the reaction time. The plot indicates that the growth has an average linear tendency of 92.9 nm/min in the interval from 6.2 to 27.8 ìm, with reaction times between 60 to 300 min. The upper points belong to the PPTh synthesized in the zones with the highest electronic energy.

Structural analysis

Figure 2 shows the IR spectra of PPTh thin films synthesized in the center zone of the reactor at different reaction times. The spectra were taken with a Perkin-Elmer FT-IR 2000 spectrophotometer applying 32 scans directly to the films without substrates or any other support. The spectra of the polymers

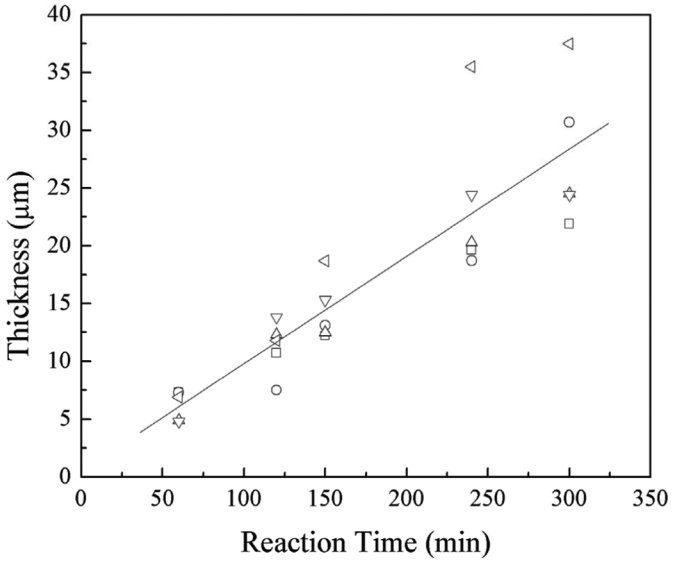


Fig. 2. Average thickness of plasma PPTh films.

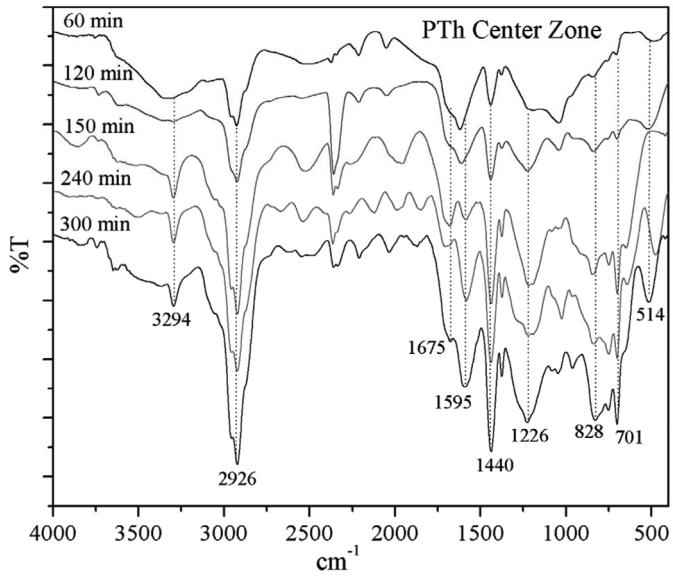


Fig. 3. FT-IR spectra of plasma PPTh.

synthesized at short reaction time presents wider absorptions than the polymers synthesized at longer reaction time.

The IR spectra show peaks at 1440 and 1226 cm^{-1}, characteristic of the thiophene ring substitutions. Considering the conditions of synthesis, the substitution indicates a growing of chains replacing hydrogen atoms in the thiophene rings with other similar rings or with other derived chemical compounds produced in the plasma. The absorption around 701 cm^{-1} can be associated to the C-S bonds of the thiophene rings.

The spectra contain two related absorptions bands at 3294 and 2926 cm^{-1}, that can be assigned to =C-H and -C-H bonds respectively, belonging to aromatic and aliphatic groups. The double bonds are part of the thiophene rings and the aliphatic

groups can be originated in some fragments of the thiophenes due to the high energy of the discharges. The absorption of -C-H groups with the reaction time increases respect to the =C-H groups, which is an indicative that the fragmentation of molecules in the reactor increases because of the continuous collisions of molecules with the most energetic particles in the plasma. When the monomer molecules break, depending on the point of rupture, the reactive fragments would be alkenes with a different level of unsaturation. During the synthesis, some of the fragments are removed from the reactor by the vacuum system but others join among them or with other thiophene reactive molecules forming complex chains of thiophenes and fragments in several combinations.

Another absorption related with unsaturation in the polymers can be seen in the peaks at 1675 and 1595 cm^{-1} associated with C=O and C=C bonds, respectively. The C=O absorption is a small shoulder that appears because of the superficial oxidation in the films due to the neutralization of the last radicals with the atmospheric oxygen. As the polymers are thin films, the oxidation of the surface could include a great part of the body. The C=C bonds belong to the alkenes discussed before.

Elemental Analysis

Figure 4 shows the elemental analysis carried out on the surface of PPTh as a function of the reaction time. The analysis was made by energy dispersive spectroscopy with a sapphire probe EDAX XL30. The elements quantified in the polymers were C, S and O. The first two elements belong to the thiophene rings; however, the source of O, as discussed before, could be the oxidation of the material by the atmospheric air after the plasma polymerization.

The atomic percentage of C varies between 52% and 54%, S was found in the range of 39-42%, and the percentage of O varies between 5 and 7%. As expected by stequiometry, the atomic C/S ratio presents an almost constant value, around 4, in all the polymerization times, while the atomic C/O ratio increases from 10.5 to 11.5 as a function of the synthesis time. This ratio can be used to represent the oxidation on the surface of the polymers that varies from 2.6 to 2.8 thiophene rings for each oxygen atom. The oxidation can be seen as proportional to the "live" free radicals on the polymers. This effect increases with the reaction time.

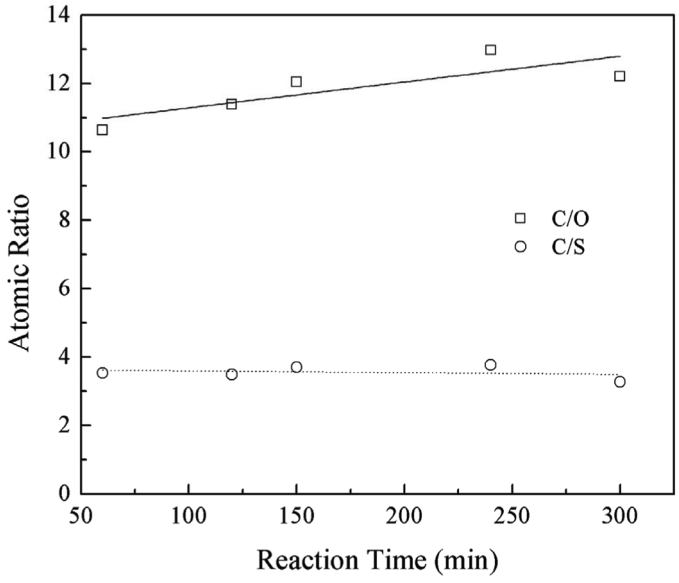


Fig. 4. Atomic ratio of PPTh.

Morphological Analysis

Figure 5 shows micrographs of the polymers taken with a scanning electron microscope Philips XL30. The films have an increasing granular morphology evolving with the reaction time. At a short synthesis time, 60 min, the polymers exhibit either a smooth texture or a light ruggedness and a stratified growing mechanism following the morphology of the surfaces where they grew. Small folds can be observed in some regions due to the effect of the electrode surface and to the solvent used when the films were separated from the surfaces, see Figure 5(a).

However, as the reaction time increases, 120 min, the films show roughness formed with small bubbles apparently emerging from the surface with diameters between 1 and 10 μm, see Figure 5(b). At longer reaction times, 150 and 240 min, some of the bubbles are almost completely formed as spheres. Many of them preserve points of union with the films, but other bubbles were released as independent particles or in agglomerates, see Figures 5(c) and 5(d). Four groups of particles with different approximate diameter can be identified in the micrograph, 285 nm, 380 nm, 500 nm and 1000 nm.

Considering the process as a function of the time of synthesis, it can be observed that initially, the polymers form thin films on the inner surface of the reactor. However, with the continuous exposure to the plasma, the films increase the thickness, but at the same time nucleate particles in bubbles with comparatively high diameter, up to 10 μm. The nucleating process affects mainly the surface. However, once the bubbles were formed, they reduce their diameter until the range of mesoparticles (100-500 nm).

Electric Conductivity

The volumetric electric conductivity of the films was calculated measuring the resistance using a two-probe device with parallel electrodes with the polymers in the middle [13]. The temperature interval varied between 60 and 100 ºC and the atmospheric relative humidity was approximately 50% in all cases. The analysis presented here was done in samples prepared with mixtures of 4 or 5 films synthesized at different positions inside the reactor to have averaged values.

The electric conductivity of PPTh was analyzed with regard to the synthesis time and temperature, which is closely related with the water content in the polymers. The interaction of polymers with water and the possible structural changes

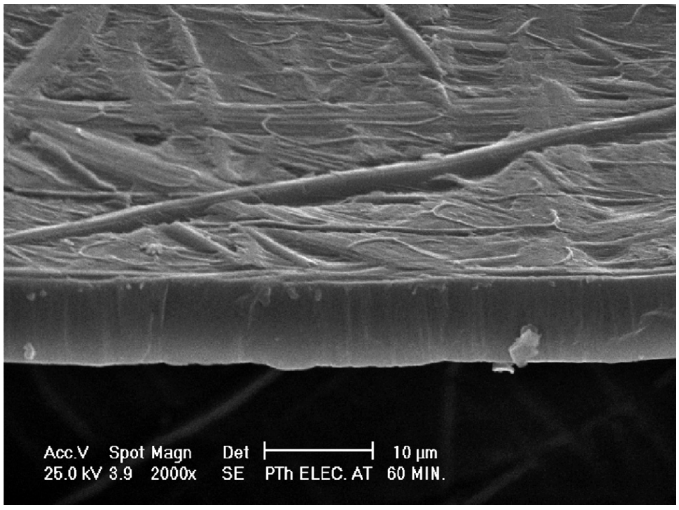


Fig. 5(a). PPTh synthesized at 60 min.

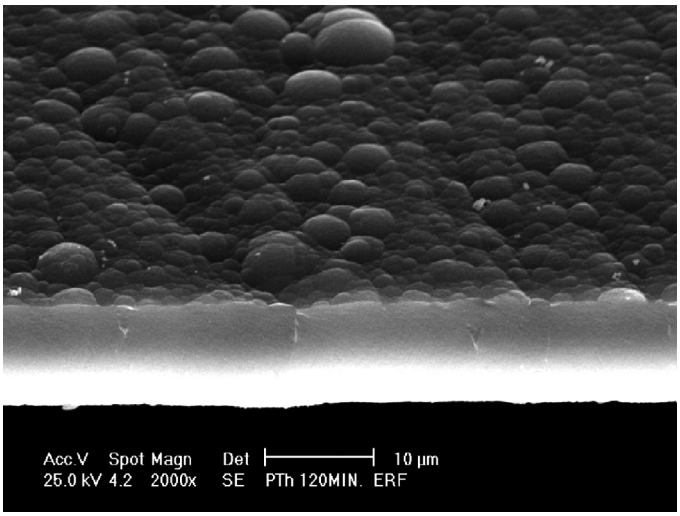


Fig. 5(b). PPTh synthesized at 120 min.

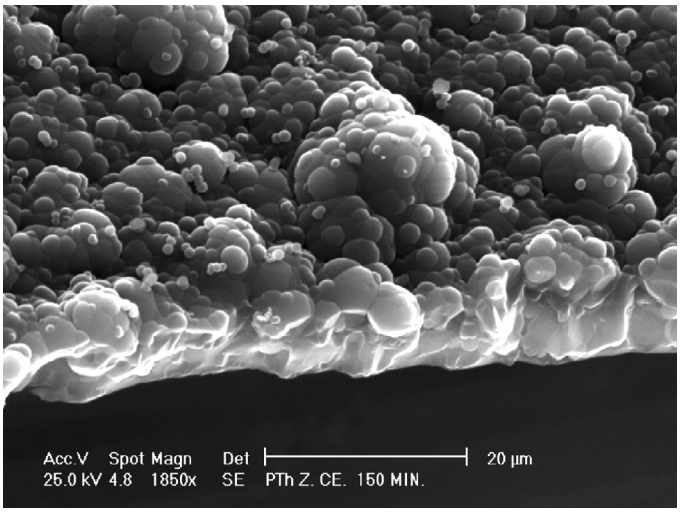


Fig. 5(c). PPTh synthesized at 150 min.

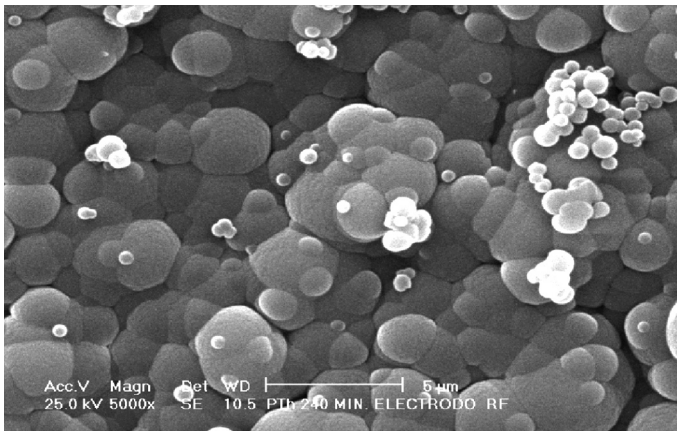


Fig. 5(d). PPTh synthesized at 240 min.

Fig. 5. Morphology of PPTh with different time of synthesis. See the evolution of the films, from a rather smooth surface to an agglomerated mesoparticle appearance.

with temperature are significant factors in the electrical properties of this polymer.

Four heating-cooling cycles were applied to PPTh during the measurement of the electrical resistance with the purpose of removing the effects of humidity and solvents in the electrical properties. The first heating process can be associated to the release of the solvents absorbed when the polymer was separated from the reactor and to the water absorbed from the atmosphere. However, after the third heating cycle, once the water and solvents are removed from the polymer, the intrinsic conductivity of the material can be calculated.

Figure 6 shows the conductivity of PPTh as a function of temperature in the first heating-cooling cycle. At shorter reaction times, the humidity in the polymers increases the conductivity by 3 or 4 orders of magnitude, see the first 3 curves in the heating step. Nevertheless, at longer reaction times, the polymers do not improve their conductivity in the same way as in the first case. They only show an increase of intrinsic conductivity with temperature.

Figure 7 shows the electric conductivity of PPTh after the third cycle of heating-cooling. The temperature interval remained between 60 and 100 °C. In these conditions, the influence of solvents and atmospheric humidity in the polymer is reduced to very low levels. It is interesting to notice that the conductivity increases with temperature for one way in the plot, but returns for another trajectory when temperature decreases, without completing a cyclic process. This effect is more intense at shorter reaction times and it has been also observed in other plasma polymers, as polyanilines and polypyrroles [13] because of modifications in the ordered segments

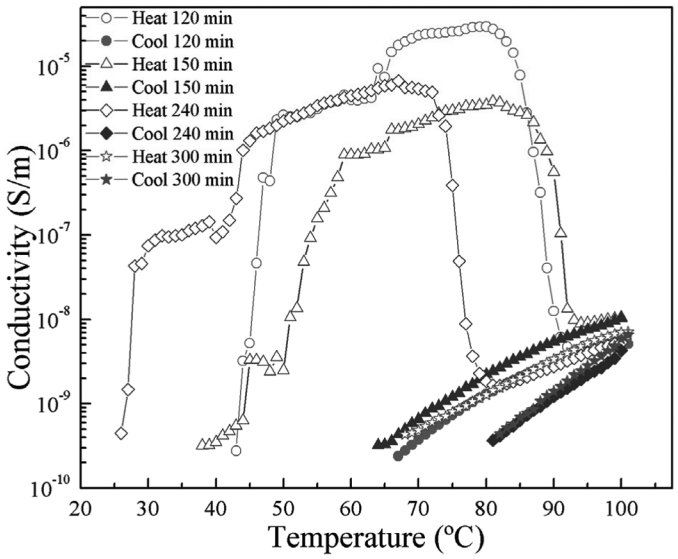


Fig. 6. Electric conductivity of PPTh with humidity.

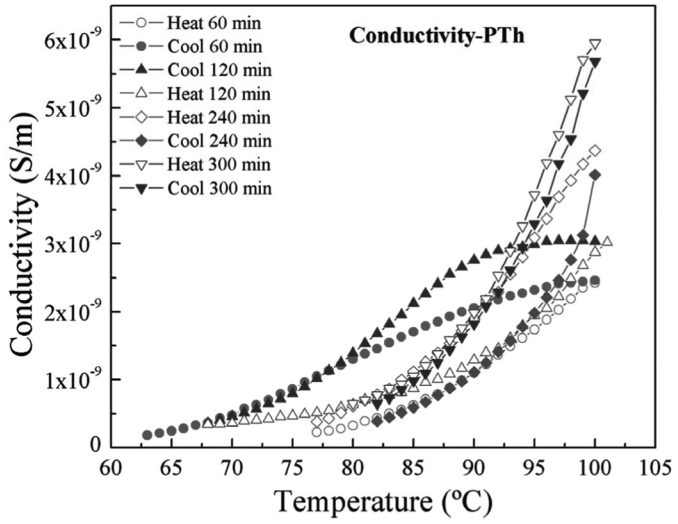


Fig. 7. Electric conductivity of PPTh without humidity.

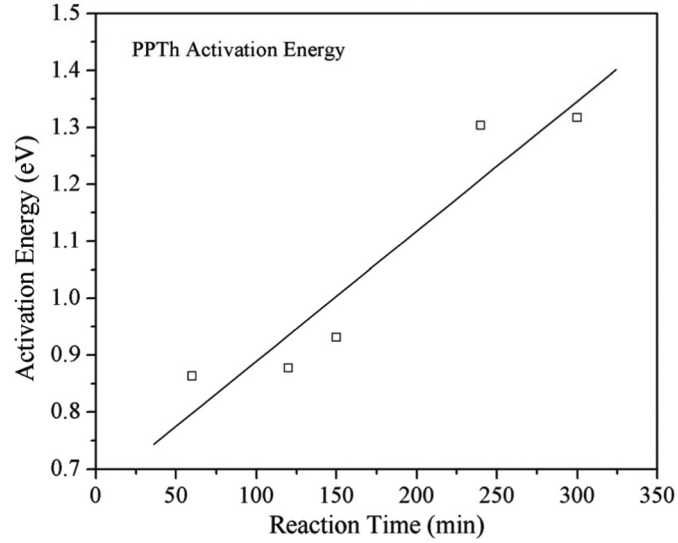


Fig. 8. Activation energy of PPTh.

in the polymers. In the case of PPTh, this phenomenon reduces at longer reaction times.

One of the important variables resulting from the electric properties of semiconductors is the activation energy (Ea). This is the initial energy that the electric charges need to move inside the material. Ea increases with temperature in insulators and semiconductors and decreases in metals. The activation energy in PPTh can be calculated from the Arrhenius formulation of conductivity with temperature. The results indicate that the tendency of the activation energy is linearly increasing with the reaction time, see Figure 8. Ea varies approximately from 0.86 to 1.35 eV with a rate of 2.28 meV/min. As Ea increases, more energy is needed to move the charges inside the structure.

Conclusions

Different polymers of thiophene can be obtained as thin films in rf resistive plasmas, whose properties show the influence of electric and thermodynamic conditions during the polymerization. The analysis of the structure of such polymers suggests that some thiophene rings break and that the fragments produce complex polymers formed with thiophene rings and fragments. This effect was more marked at longer plasma exposures.

The combinations of multiple chemical reactions during the polymerization were reflected in the morphology of the films that increased the roughness along the synthesis time. The films followed a trend from a smooth surface at low exposure time, the formation of some bubbles on the surface at longer plasma exposure, and finally the formation of particles of different diameter, from approximately 300 nm to 1000 nm. The average total film thickness had a linear tendency increasing with the synthesis time at a rate of 93.2 nm/min.

The electric conductivity was not significantly influenced by the synthesis time. However, the values did show a strong dependence on another variable, the water content in the polymer. The intrinsic conductivity varied from 10^{-10} to 10^{-8} S/m, but the influence of the residual solvents and mainly the water content in the polymers increased this conductivity up to 10^{-5} S/m.

The electronic activation energy derived from the intrinsic conductivity had a linear tendency increasing with the synthesis time between 0.56 and 1.41 eV. With these values, PPTh is positioned in the range of semiconductors because of the range of the activation energies, but not for their intrinsic conductivity.

Experimental

The experimental setup for the plasma polymerization of thiophene is shown in Figure 9. The conditions for the polymerization were achieved by rf glow discharges at 13.5 MHz. The experimental arrangement was approximately the same as that used in other works [11, 12]. The reactor was formed

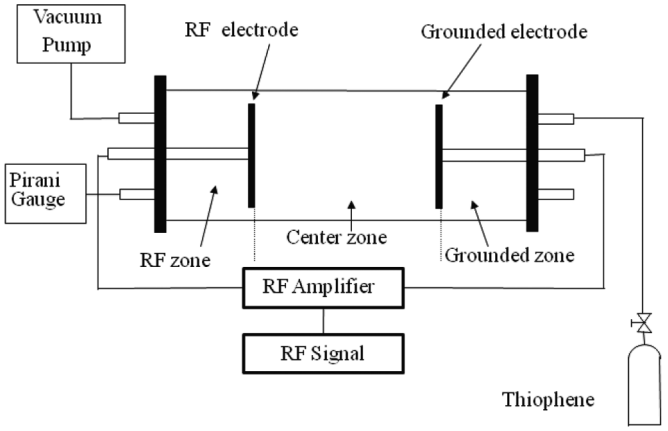


Fig. 9. Experimental setup for the synthesis of PPTh.

by a glass tube, 21 cm long and 9 cm in diameter, with 2 stainless steel flanges at the ends. The electrodes were 6.5 cm in diameter, also made of stainless steel, separated by 12 cm. One electrode was polarized with the rf signal and the other was grounded, as a reference. The pressure inside the reactor was 10^{-2} torr. Thiophene was fed to the reactor in vapor phase. Polymerizations by 60, 120, 150, 240 and 300 min were performed at 10 W in all cases.

As the chemical reactions involve electrical discharges in resistive mode, the continuous flow of charges can increase the temperature of the reactor promoting the decomposition of the polymers in progress if the temperature rises excessively. The highest temperatures could be in the central region between the electrodes, where the main flow of charges occurs, and the lowest in the glass walls of the reactor. To reduce the undesirable effects of high temperatures, the reactor was cooled with 2 fans to keep the temperature of the external walls below 50 ºC.

The polymers were formed on the reactor walls and on the electrodes and they were separated from the surfaces by applying ethanol, methanol, acetone, and distillated water. The solvents dissolved and separated some of the low molecular weight compounds generated in the synthesis. However, the remaining solids were thin films of polymers that could not be dissolved or separated in other fractions. They were only swelled with the solvents used.

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References

1. Subramanian, H.; Lagowski, J. B. *Int. J. Quant. Chem*. **1998**, *66,* 229-240.
2. Granström, M. *Polym. Adv. Technol*. **1979**, *8*, 424-430.
3. Schon, J. H.; Dodabalapur, A.; Bao, Z.; Kloc, C.; Schenker, O.; Batlogg, B. *Nature* **2001**, *410*, 189-192.
4. Bhat, N. V.; Wavhal, D. S. *J. Appl. Polym. Sci*. **1998**, *70*, 203–209.
5. Ryan, M. E.; Hynes, A. M.; Wheale, S. H.; Badyal, J. P. S. *Chem. Mater*. **1996**, *8*, 916-921.
6. Silverstein, M. S.; Visoly, F. I. *Polymer* **2002,** *43*, 11-20.
7. Yu, Y. J.; Kim, J. G.; Boo, J. H. *J. Mater. Sci. Lett.* **2002**, *21*, 951-953.
8. Groenewoud, L. M. H.; Weinbeck, A. E.; Engbers, G. H. M.; Feijen, J. *Synth. Met.* **2002**, *126*, 143-149.
9. Groenewoud, L. M. H.; Engbers, G. H. M.; Feijen, J. *Langmuir* **2003**, *19*, 1368-1374.
10. Groenewoud, L. M. H.; Engbers, G. H. M.; Terlingen, J. G. A.; Wormeester, H.; Feijen, J. *Langmuir* **2000**, 16, 6278-6286.
11. Cruz, G. J.; Morales, J.; Castillo-Ortega, M.; Olayo, R. *Synth. Met.* **1997**, *88*, 213-218.
12. Cruz, G.J.; Morales, J., Olayo, R. *Thin Solid Films* **1999**, *342*, 119-126.
13. Morales, J.; Olayo, M. G.; Cruz G. J.; Castillo-Ortega, M. M.; Olayo, R. *J. Polym. Sci., Polym. Phys.* **2000**, *38*, 3247-3255.