

Radiofrequency power behaviour of low pressure triglyme plasmas

Comportamento de plasmas de triglime com a potência de rádiofrequência aplicada à baixa pressão

Antonio Renato Bigansolli¹, Roberto Yzumi Honda², Maurício Antônio Algatti², Rogério Pinto Mota², Milton Eiji Kayama²

ABSTRACT

Plasma polymerization of ethylene glycol monomers obtained from RF-excited low temperature plasma is promising technique for obtaining non-fouling hydrophilic biocompatible surfaces that may be used in many scientific and technological applications. The use of plasma diagnostics for optimizing the processes is an important issue to be addressed on plasma materials processing for customized biomedical applications. This paper deals with the RF power dependence of different chemical species in low pressure RF-excited $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ tri-ethylene glycol di-methyl ether (triglyme) plasmas for different values of pressure. The RF-power was coupled to the plasma chamber through an appropriate matching network in order to optimize the process. The RF power was varied from 5 to 45 watts. The results showed that the population of different chemical species resulting from monomer fragmentation presents a strong dependence on RF power. It can be seen that the population of heavier species decrease with RF power followed by the increasing of the lighter one. This result is in close agreement with the increase of electron temperature at higher RF power levels. Therefore one can conclude that the monomers functionality is preserved within the plasma-deposited thin films if the RF power is kept in low levels during the process.

Keywords: Plasma; Triglyme; Radiofrequency; Pressure.

RESUMO

Polimerização à plasma de monômeros de etileno-glicol obtidos por excitação de rádio frequência em plasmas de baixa temperatura é uma técnica promissora para a obtenção de superfícies "non-fouling", (superfícies repelentes à adesão de microorganismos), em materiais biocompatíveis hidrofílicos que podem ser utilizados em aplicações científicas e tecnológicas. O uso de diagnósticos à plasma para a otimização dos processos é uma questão importante a ser abordado no processamento de materiais à plasma para aplicações biomédicas. Este trabalho descreve a dependência da energia das populações de diferentes espécies químicas com a potência de Rádiofrequência - RF acoplada em plasmas de baixa pressão de $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ tri-etileno-glicol di-metil éter (triglime) para diferentes valores de pressão. A potência de RF foi acoplada ao reator de plasma através de um sistema apropriado, a fim de otimizar o processo. A potência de RF foi variada de 5 a 45 watts. Os resultados mostraram que as populações das diferentes espécies químicas resultantes da fragmentação do monômero apresentam uma forte dependência com a potência de RF aplicada ao plasma. Pode ser visto que as populações das espécies mais pesadas diminuem com o aumento da potência de RF aplicada. Este resultado se encontra em concordância com o aumento da temperatura dos elétrons a níveis mais elevados da potência de RF aplicada. Podemos, portanto, concluir que a funcionalidade do monômero é preservada nos filmes finos depositados à plasma se a potência de RF aplicada for mantida em níveis baixos durante o processo.

Palavras-chave: Plasma; Triglime; Rádiofrequência; Pressão.

¹Universidade Federal Rural do Rio de Janeiro – Instituto de Tecnologia – Departamento de Engenharia Química – Seropédica (RJ), Brazil.

²Universidade Estadual Paulista Júlio de Mesquita Filho – Faculdade de Engenharia de Guaratinguetá – Departamento de Física e Química – Guaratinguetá (SP) - Brazil.

Correspondent author: Antonio Renato Bigansolli – Universidade Federal Rural do Rio de Janeiro – Instituto de Tecnologia – Departamento de Engenharia Química – CEP 23890-000 – Seropédica (RJ) Brazil

E-mail: bigansolli@ig.com.br

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INTRODUCTION

Materials processing by low pressure RF excited plasmas are of great importance in many technological and scientific issues encompassing microelectronics, biomaterials industry⁽¹⁻⁷⁾ and more recently the field of nanoscience and nanotechnology^(8,9). The main reason is that within such kind of plasmas electrons can attain an energy excess of some eV in comparison with the heavy species present within discharge. This thermal non-equilibrium situation is highly favourable to molecular fragmentation process by electronic impact, giving rise to a very reactive chemistry in a relative cold environment⁽³⁾ whose kinetics is not easily controlled. Therefore is of great importance to set several plasma diagnostics in order to probe the trends of chemical species as well as the electrons for different plasma parameters such RF power coupled to the plasma chamber, gas pressure, gas flux and so on⁽¹⁰⁻¹³⁾.

In the field of biomaterials science, plasma polymerized polyethylene glycol dimethyl ether is a material that has been keeping the attention of the scientific community due to its non fouling characteristics⁽¹⁴⁻¹⁷⁾. If the appropriate plasma parameters are set these films may be synthesized keeping a molecular structure similar to the polyethylene oxide-like (PEO-like) with the advantage that these films are not soluble in water. The aqueous solubility of PEO makes it inappropriate for many biomaterials applications. In order to keep the monomer structure within the plasma deposited films and consequently its functionality, many different approaches have been addressed in literature as for instance the film deposition under low mean RF power level by controlling the power supply on/off ratio^(12,18), the decreasing of monomer residence time and consequently the reduction of its interaction with the plasma environment⁽¹⁸⁾, the cooling of substratum with liquid nitrogen⁽¹²⁾, the energy reduction of the ions reaching the substratum⁽¹³⁾, and so on.

In order to investigate which set of plasma parameters would result customized films in plasma polymerization of PEO-like coatings this paper deals with the study of the RF power dependence of several different chemical species resulting from triglyme fragmentation for different values of the pressure inside the reactor. The trends of several chemical species were analyzed by mass spectrometry in the power and

pressure range from 5 to 45 W and 120 mTorr to 300 mTorr respectively.

EXPERIMENTAL SETUP AND PLASMA DIAGNOSTICS

Plasmas were generated by a RF power supply operating in the range from 5 to 45 W in $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$ (triglyme) atmospheres varying from 120 mTorr to 300 mTorr within a stainless steel cylindrical, 210 mm of internal diameter and 225 mm long, parallel plate electrodes plasma reactor. The chamber has eight lateral entrances, positioned at the midway between the electrodes that can be used for optical, electrical and mass diagnostics and for coupling the low (mechanical pump) and high (turbo-molecular pump) vacuum systems. The vacuum inside the plasma chamber was monitored by piraniTM (thermocouple) and penningTM (inverse magnetron) gauges. The turbo-molecular pump is assembled to the chamber through a gate valve and was used for cleanness purposes. The pressure was pumped down to 10^{-6} Torr. The plasma reactor was purged with argon several times before execution of the experiment. Plasma chamber walls were heated with a temperature controlled belt for minimizing monomer's condensation as well as the humidity. Triglyme monomer (99.99% of purity) was put inside a heated stainless steel bottle and was fed into the plasma chamber through a needle valve. Plasma was excited by a RF power supply operating in 13.56 MHz whose output intensity could be varied from 0 to 300 W (Tokyo HY-Power model RF-300TM). The RF power was coupled to the plasma reactor through an appropriate matching network (Tokyo HY-Power model MB-300TM) that allowed one to minimize the reflected RF power. The mass spectrometry was performed using a mass spectrometer and energy analyzer (Hiden Analytical model EQP-300TM), operating in the mass and energy range from 1 to 300 amu and from 0 to 100 eV respectively. The optical spectra were collected using a computer controlled 2 m focal distance plane grate spectrometer provided with a photomultiplier operating in the spectral range from 800 nm to 250 nm (Hamamatsu model R374). The block diagram of the experimental setup is presented in Fig. 1.

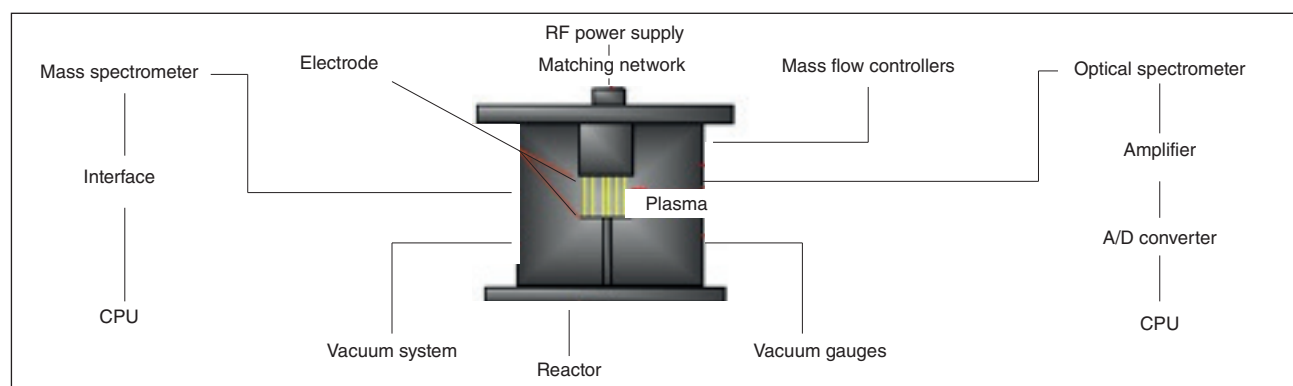


Figure 1: Block diagram of the experimental set-up.

RESULTS AND DISCUSSION

Table 1 presents all possible triglyme (178 amu) primary fragments resulting from the break-up of chemical bonds between carbon-carbon and carbon-oxygen atoms. Since triglyme molecule is central symmetric to the chemical bond between carbon-carbon atoms located in the ethylene-glycol group one may identify only six different points of molecular rupture involving the above mentioned chemical bonds which result the fragments listed in Table 1. It should be pointed out that all molecular fragments, presented in Table 1, with the exception of number 11 (163 amu), may result also from secondary or higher order fragmentation process of the more heavy fragments of triglyme molecule. The number of possibilities contributing for the population of a fragment increases inversely proportional to its mass. From the point of view of the non-fouling characteristic of plasma deposited triglyme films, the ethylene-glycol structure, e.g., $\text{CH}_2\text{CH}_2\text{O}$ (44 amu), is one the most important structure to be retained within the film composition if one wants to keep its functionality^(4,6). Therefore is important to keep under control the plasma parameters that enhance the presence of heavy triglyme fragments within the discharge instead of the light ones.

Figure 2 shows the RF power dependence of triglyme's fragments within the plasma, for a fixed pressure of 120 mTorr. The trends reveal the decreasing of heavy species counting rate with the RF power increasing. This behavior may be attributed to the predominance of inelastic electronic collisions resulting in molecular fragmentation. It also can be appreciated that the population of light species like for instance CH_3OCH (44 amu) increases with the increasing of the RF power. This result is in agreement with the decreasing of the concentration of the heavy species within the plasma discharge.

Figure 3 shows the results obtained at a fixed pressure of 300 mTorr. One can see that the trends of different chemical species are quite similar to the presented in Fig. 2. It is seen that only the particle's counting rate decreased with the increasing of the pressure from 120 to 300 mTorr. This feature of the trends indicates that the pressure increasing was not enough to change

significantly the electronic mean free path as well as the electronic mean kinetic energy. The increasing of the mean electronic kinetic energy certainly would result the production of different chemical species due electronic inelastic collisions.

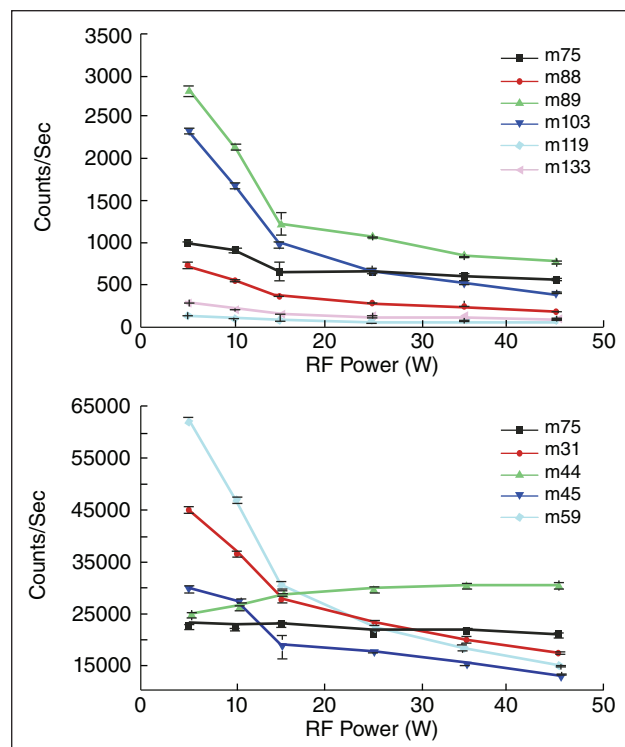


Figure 2: RF power dependence of triglyme fragments at a fixed pressure of 120 mTorr.

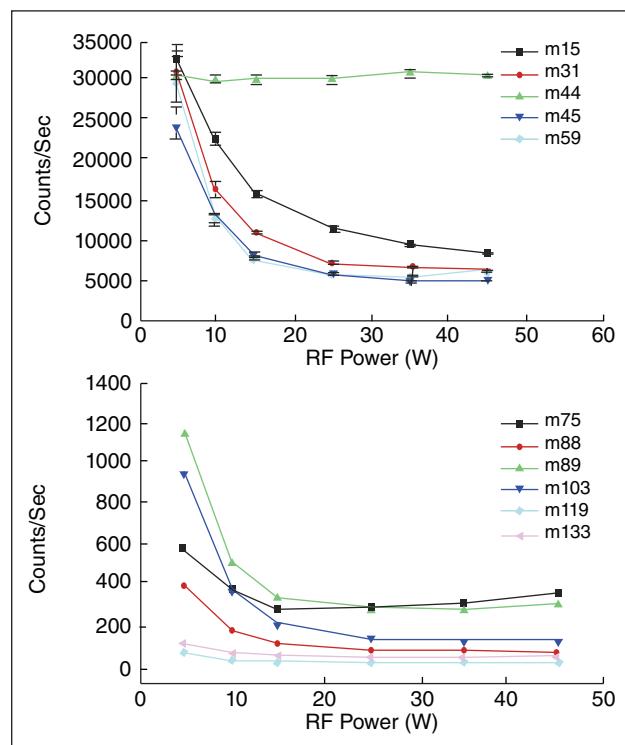


Figure 3: RF power dependence of triglyme fragments at a fixed pressure of 300 mTorr.

Table 1: Primary Triethylene-glycol-dimethyl-ether fragments.

| Fragment | Chemical structure | Mass (amu) |
|----------|--|------------|
| 1 | CH_3 | 15 |
| 2 | CH_3O | 31 |
| 3 | CH_3OCH_2 | 45 |
| 4 | $\text{CH}_3\text{OCH}_2\text{CH}_2$ | 59 |
| 5 | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}$ | 75 |
| 6 | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2$ | 89 |
| 7 | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ | 103 |
| 8 | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$ | 119 |
| 9 | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ | 133 |
| 10 | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$ | 147 |
| 11 | $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$ | 163 |

Figure 4 show the pressure dependence of triglyme fragments for different values of the applied RF power to the plasma chamber. It can be seen that there is an optimum pressure value for each RF power level. It is also observed that the increasing of RF power applied to the discharge caused a significant reducing of several different chemical species within the discharge. This fact probably is directly related to the decrease of the mean free path of the particles within the plasma that results a higher rate

of species recombination. The trend behaviour of the pressure dependence of triglyme fragments allows one to consider that up to 200mTorr the mean free path is small enough to allow the process of primary monomer's fragmentation. The further increasing of pressure reduces the mean free path of different species enhancing the occurrence of secondary fragmentation processes. This fact explains the reduction of primary species within the plasma.

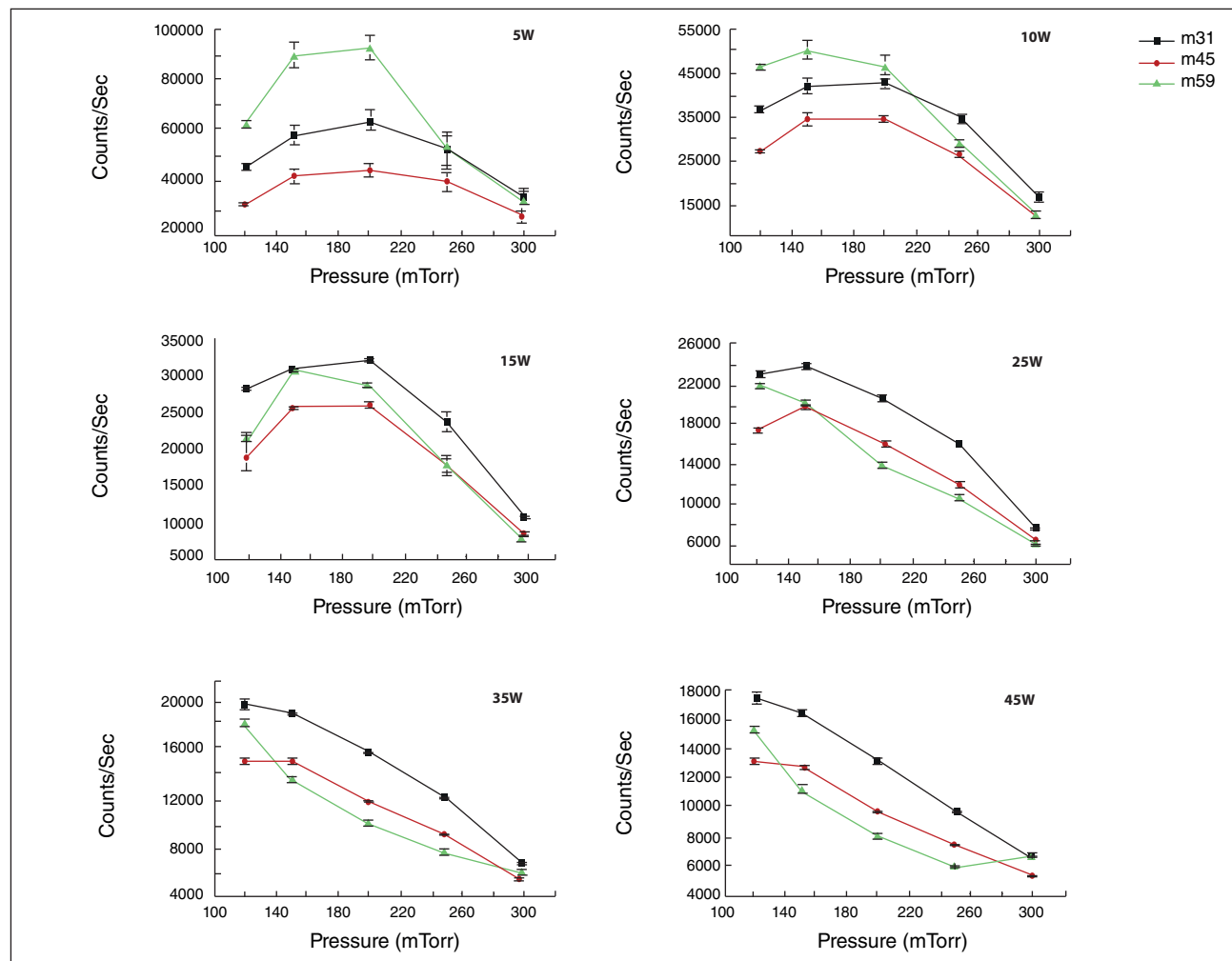


Figure 4: Pressure dependence of triglyme fragments for different RF power values.

CONCLUSIONS

The experimental results allow one to conclude that the operation of the plasma reactor at low RF power levels is appropriate if one wants to preserve the monomer functionality at the plasma polymerized films obtained from triglyme plasmas. The low RF power level minimizes molecular fragmentation enhancing the occurrence of heavy chemical species within the discharge. These heavy species may be incorporated to the polymeric film structure preserving the monomer functionality. The results also show that mass spectrometry can be used for monitoring the production of customized plasma polymerized PEO-like structures that may be used as a non-fouling surface in biomaterials applications⁽¹⁻⁴⁾.

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