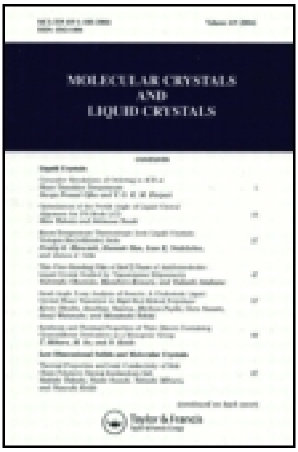

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Optical and Structural Properties of PEO-Like Plasma Polymers

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Version of record first published: 29 Oct 2010

To cite this article: Rogério Pinto Mota, Antonio Renato Bigansolli, Érica Freire Antunes, Elidiane Cipriano Rangel, Nilson Cristino Da Cruz, Roberto Yzumi Honda, Mauricio Antonio Algatti, Emilia Akemi Aramaki & Milton Eiji Kayama (2002): Optical and Structural Properties of PEO-Like Plasma Polymers, Molecular Crystals and Liquid Crystals, 374:1, 415-420

To link to this article: http://dx.doi.org/10.1080/713738263

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 415-420

1058-725X/02 $12.00 + .00

Optical and Structural Properties of PEO-Like Plasma Polymers

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This paper deals with the study of optical, structural and biocompatible properties of PEO-like plasma polymerized films resulting from RF excited diethylene glycol dimethyl ether ($CH_3O(CH_2CH_2O)_2CH_3$ diglyme) glow discharges. The study was carried out using visible-ultraviolet and FTIR spectroscopies and contact angle measurements. FTIR spectra of plasma polymerized diglyme showed a stronger presence of ethylene glycol groups in film structure for lower RF power levels. The contact angle measurements for water revealed an increasing from 30^0 to $62{,}5^0$ when the RF power was varied from 2 to 45 W, indicating the decreasing of the hydrophilic character of diglyme films with the increasing of RF power. This trend is in agreement with FTIR results. The data from visible-ultraviolet reflectance and transmittance spectra revealed alterations on optical properties of plasma polymerized diglyme films. The film's optical gap varied from 3.8 to 3 eV for RF power running from 5 to 45 W.

Keywords Optical-gap; Contact-angle; Diglyme-plasmas; Diglyme-coatings; Plasma-polymers

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INTRODUCTION

Plasma materials processing by low pressure RF excited glow discharges is of key importance in many current technological issues encompassing microelectronics and biomaterials industry[1-5]. The main reason is that within such kind of plasmas electrons may attain an energy excess of some eV in comparison with the heavy particles present in the discharge. This unusual thermal non-equilibrium situation is extremely profitable in molecular fragmentation by electronic impact, giving rise to a very react- ive chemistry in a relative cold environment[1-3] whose kinetics is not easily controlled. In spite of these characteristics plasma polymerized films with customized properties may be synthesized within such kind of discharges.

In the field of biomaterials science, plasma polymerized poly-ethylene glycol dimethyl ether is an issue that has been keeping the attention of the scientific community due to its non fouling characteristic[4-10]. 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 less appropriate for many biomaterials applications. In order to set the appropriate experi-mental parameters that would result customized film structures in plas-ma polymerization of PEO-like coatings this paper deals with plasma polymerization of diglyme for different values of the RF power. The retention of the monomer structure within the films for a fixed pressure and different values of RF power was studied using FTIR spectroscopy. The hydrophilic character of the films deposited under different values of RF power was investigated through contact angle measurements with water as probe liquid. The optical gap of the plasma polymerized digly- me films obtained for different values of RF power was calculated from the visible-ultraviolet reflectance and transmittance spectra.

EXPERIMENTAL SETUP AND MEASUREMENTS

The glow discharges were generated by a RF power supply operating in the range from 2 to 45 W in $CH_3O(CH_2CH_2O)_2CH_3$ (diglyme) atmospheres for a fixed pressure of 16 Pa within a cylindrical stainless steel, 210 mm of internal diameter and 225 mm long, parallel plate electrodes plasma reactor. The vacuum inside the plasma chamber was monitored by pirani™ (thermocouple) and penning™ (inverse magnetrom) gauges. The turbo-molecular pump was coupled to the chamber through a gate valve and was used for cleanness purposes. The pressure was pumped down to 1.33×10^{-5} Pa being the chamber purged with argon several times before each running of the experiment. The plasma chamber walls were heated with a temperature-controlled belt in order to minimize the monomer condensation as well as the humidity.

Diglyme placed inside a stainless steel bottle was fed into the plasma chamber through a needle valve. Diglyme plasmas were 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-300™). The RF power was coupled to the plasma reactor through an appropriate matching network (Tokyo HY-Power model MB-300™).

The FTIR spectra for diglyme films deposited at 16 Pa for differ- ent values of the RF power was collected by a FTIR spectrometer Jasco 410™ operating in the spectral range from 4000 cm^{-1} to 400 cm^{-1}.

The contact angle measurements were performed using a compu- ter controlled goniometer Ramé Hart model 100-00™ that allows the measurement of the angle formed between the surface and the liquid drop with a maximum precision of 3^0. The transmittance and reflectance spectra were collected by a visible-ultraviolet spectrometer Hitachi U-3501™ operating in the spectral range varying from 200 to 600 nm.

RESULTS AND DISCUSSIONS

Figure 1 shows the FTIR spectra of diglyme films, in the spectral range from 4000 to 400 cm^{-1}, for different values of the RF power coupled to the plasma chamber, e.g., 2, 10 and 35 W. One may distinguish several different absorption bands in these spectra. The spectral range between 3600 and 3300 cm^{-1} is characterized by OH group's absorption whose intensity increases with the increasing of the RF power. In spite of the fact that the chemical bond O-H is not present in the monomer structure, it appears in the polymeric film probably due the fragmentation and recombination processes within the plasma discharge. Two others sources that contribute for the retention of oxygen in diglyme films are the reactions with residual water vapor inside the plasma chamber and the recombination process of oxygen present in the air with the free radicals at the film's surface when it is exposed to the external environ-ment.

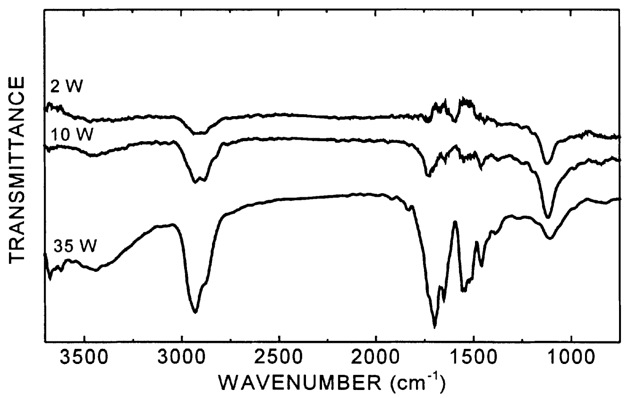

FIGURE 1 FTIR spectra of plasma-polymerized diglyme.

The spectral range between 3000 and 2800 cm^{-1} shows the presence of C-H bonds that may be identified as C-H stretching in CH_2 and CH_3 groups. The increasing of CH_2 and CH_3 group's concentrations in the film's structure with the RF power coupled to the discharge indicates the occurrence of polymeric structures much more cross-linked. The same trend is also corroborated by the bands present in the spectral range between 1800 and 1400 cm^{-1} that may be assigned to C=O and C=C bonds resulting from recombination process within the plasma discharge. It may be pointed out that the decreasing of band intensity in the spectral range between 1250 and 1000 cm^{-1}, assigned to C-O-C and C-O structures, occurs due the increasing of monomer's fragmentation processes with the increasing of RF power coupled to the discharge.

Therefore if one intends to retain the PEO-like structures within the plasma-polymerized diglyme one should operate the plasma reactor at relatively low RF power levels.

Figure 2 shows that the contact angle for water increases from 30^0 to $62,5^0$ when the RF power was varied from 5 to 45 W, indicating the decreasing of the hydrophilic character of diglyme films with the increasing of RF power. The deposition of polymeric films at high RF power levels produces structures highly cross-linked with reduced quantity of free radicals, which effectively contributes for the increasing of the contact angle. It also may be pointed out that the exposure of polymeric structure to the external environment also contributes for the increasing of the contact angle due the recombination process with O present in air.

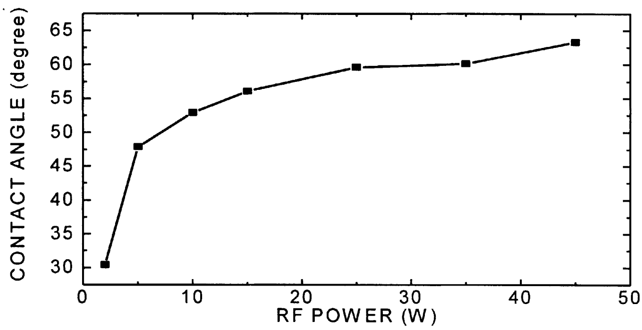

FIGURE 2 Water contact angle for plasma-polymerized diglyme.

Figure 3 shows the transmittance spectra of plasma-polymerized diglyme for different values of RF power. It may be appreciated that the transmittance decreases with the increasing of RF power. This fact is in agreement with the results obtained from FTIR spectroscopy. The increasing of molecular cross-linking decreases the polymeric optical gap due the abundance of σ and π bonds in C=C and C=O structures. These results also suggest that if one wants to produce transparent films with hydrophilic character one may operate the plasma chamber at low power levels.

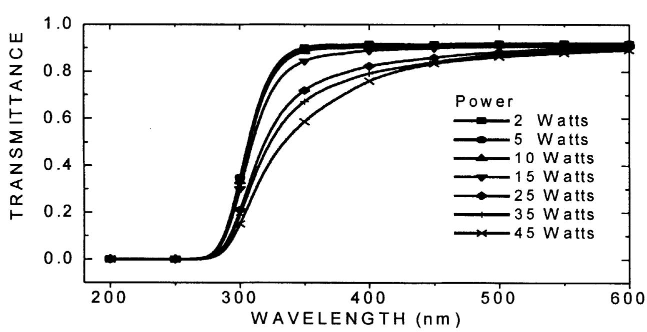

FIGURE 3 Visible-ultraviolet spectra for plasma-polymerized diglyme.

CONCLUSIONS

The presented results allow one to conclude that customized transparent and hydrophilic plasma polymerized diglyme films may be obtained from operation of the plasma chamber at low RF power levels. These transpa-rent hydrophilic polymeric films with non-fouling properties present promising applications in biomaterials industry.

ACKNOWLEDGMENTS

The authors would like to thank FAPESP, (Fundação de Amparo à Pesquisa do Estado de São Paulo) for financial support and José Benedito Galhardo for technical assistance during the plasma chamber construction.

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