

## POSSIBILITIES OF VINYL POLYMERS OBTAINMENT IN COLD PLASMA\*

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In the paper there are presented data concerning the syntheses in cold plasma conditions of vinyl polymers. The new synthesised structures are characterized from the viewpoint of some physico-chemical properties.

As a consequence of the realized structure (network) the synthesised polymers are proposed as a matrix for bioactive substances.

*Key words:* plasma polymerisation, vinyl polymers, network.

### 1. INTRODUCTION

Plasma polymerization is a procedure, in which gaseous monomers, stimulated through plasma, condense on freely selectable substrates, as high cross-linked layers. As the monomer molecules in plasma, for the most part, become shattered into reactive particles, there remain at most, only partially preserved chemical structures of the output gases in the product, which results in cross-linked and disordered structure. Structural preservation and cross-linking gradients can be controlled through process parameters, such as pressure, working gas-flow and applied electrical output; so that, one can also construct so called gradient layers; with increasing degree of cross-linking over the thickness [1–4].

Plasma processes provide a cost effective and environmentally friendly alternative to many important industrial processes because the method produces no unwanted waste products and in most cases exposes operators to no significant hazards. Plasma pretreatment is a vital process used for improving lamination, printing, and adhesion. Plasma promotes adhesion by increasing the effective surface area of the metals for example. This roughening

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in turn promotes more intimate molecular contact between the metal and the adhesive allowing for stronger bonds to occur. The highly reactive ions found in plasma make the processing a valuable tool in surface cleaning. Additionally plasma etching is a tool used in the semiconductor industry to create tunnels on surfaces [5–9].

Plasma polymerization is a relatively new material preparation process involving the deposition of ultra-thin-films under the influence of a partially ionized gas. Plasma polymerized films are candidates for use in both dye-doped optical limiters and thin film optical interference filters, due to the variety of organic precursors used, and to their low temperature processing [10].

Organic vapors can be polymerized at low temperatures using plasma enhancement. Plasma polymerization can also be used to produce polymer films of organic compounds that do not polymerize under normal chemical polymerization conditions because such processes involve electron impact dissociation and ionization for chemical reactions. Plasma polymerization takes place in a low pressure and low temperature plasma that is produced by a glow discharge through an organic gas or vapor. Plasma polymerization depends on monomer flow rate, system pressure and discharge power among other variable parameters such as the geometry of the system, the reactivity of the starting monomer, the frequency of the excitation signal and the temperature of the substrate. Glow discharge polymerization of organic compounds seems to proceed by the free radical mechanism and the extent of ionization is small. The combination and recombination of these radicals form high molecular weight compounds called polymers. The free radicals are trapped in these films, which continue to react and change the polymer network over time [11–13].

Additionally, any gases in a reaction vessel (*i.e.* nitrogen and oxygen) may be activated into their corresponding radicals and may be incorporated into the films by radical recombination reactions. Consequently, polymers formed in plasmas generally have complex, highly crosslinked structures due to the large number of reaction pathways available during plasma excitation

In this work we are presented data concerning the syntheses in cold plasma conditions of vinyl polymers, with the presentation of some of their physico-chemical properties. As a consequence of the realized structure (network) the polymer will be used as a matrix for bioactive substances.

## 2. EXPERIMENTAL PART

### 2.1. MATERIALS

The monomers styrene ( $c > 99$  wt %, Fluka) and methyl methacrylate ( $c = 99$  wt %, Merck) were freshly distilled before use.

## 2.2. THE PLASMA INSTALLATION

Plasma is created when a neutral gas is given sufficient energy from an electronic discharge source to create new product ions and radicals. The source of free electrons is generally a high-energy glow discharge such as a high voltage electrode. These resulting collisions of electrons and gas molecules result in a net energy transfer to the molecules producing metastable fragments and energized ions. The resulting product is a mixture of highly excited ions consisting of fragmented portions of the parent molecule. The plasma particles are extremely unstable and their energetic states cause them to be highly reactive with particles or surfaces that they contact. Plasma is generally produced in a low-pressure environment using a high vacuum system to promote stability of ionic radicals formed. This low pressure stability is achieved by effectively increasing the mean free path between the active components.

For the plasma polymerization was constructed a plasma reactor (Fig. 1):

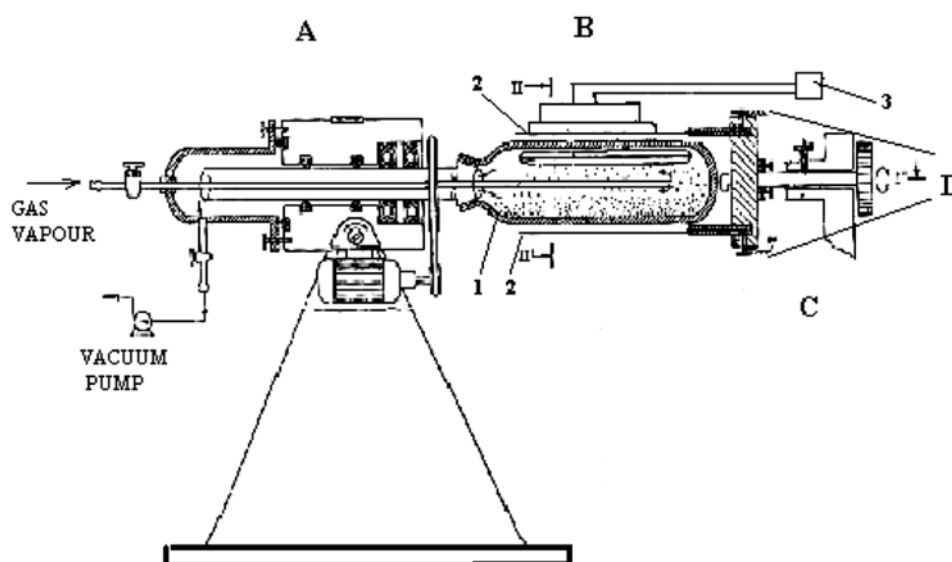


Fig. 1. – Installation for plasma polymerisation [14]: A – system for gas feeding, rotation training and vacuum; B – reaction vessel; C – system for electrodes fixing; D-HF generator; 1– rotative cylindrical reactor; 2 – semicylindrical electrodes; 3 – current supply.

The parameters of installation are: frequency = 1.5 MHz, irradiation power = 40 W, tension field = 100 V/cm, pressure = 3– 4 torr.

The plasma installation for the polymerization system consists mainly of a high frequency source, a horizontal vacuum chamber of the reactor which is a Pyrex glass cylindrical column, the vacuum pump and pressure gauge. This vacuum chamber is evacuated before each run and subsequently filled with a

specific monomer. The monomer was introduced from the gas inlet during the plasma polymerization. The discharge is obtained between two semicylindrical-shaped electrodes placed on the exterior walls of the reactor and connected to the high frequency power generator operating at 1.5 MHz. The operating pressure was adjusted by the monomer flow rate. The plasma polymerization time was 1, 2, 3, 5, respectively 10 min. After that, the polymer resulted was precipitated with acetone and dried.

### 2.3. METHOD OF INVESTIGATION

The polymeric materials were characterized by *FTIR spectroscopy* (on a DIGILAB, Scimitar Series, USA, spectrophotometer, the resolution recording was  $4\text{ cm}^{-1}$ ). For following the plasma polymerization effects on the macromolecular chains it is kept constant the amount of polymer (3 mg) in the KBr tablet (500 mg).

The structure of polymers synthesized in plasma was evidenced on the micrographs obtained by means of a *scanning electron microscope* BS 301 TESLA type (SEM). The samples were fixed with electrostatic paste on special supports. For the contrast enhancement there were first carbon coated (by thermal evaporation) and then there were metallized with gold (cathode pulverization). The laying down of gold was carried out using evaporation of the metal under a high vacuum, to give a thickness of around 15–20 Å.

### 3. RESULTS AND DISCUSSIONS

Since radicals are formed by fragmentation of monomer, some elements and groups may be absent in resulting polymer. The degree of fragmentation depends on electron density or input power and monomer flow rate. Cross-linking reactions occur on the surface or in the bulk of the newly forming plasma polymer between oligomers. The film may also change due to reaction with oxygen and water vapour in atmosphere. Although, the polymer deposition rate is linearly dependent on the current density, the minimum wattage necessary for the plasma polymerization of a given monomer differs significantly from another. This is because discharge power needed to initiate glow discharge varies from one monomer to another. The cross-linking in plasma polymer increases with the intensity and energy of bombarding ions. If the inter-electrode distance is too large, then, at a given applied potential, the local electric field in the plasma will be too low to deliver sufficient energy to the electrons. The atoms in a vacuum travel in straight lines. If there is residual gas in the chamber, the atoms will collide with the gas and would go in all directions losing some energy as heat. At higher pressures, the collisions will cause atoms to condense in air before reaching the substrate surface giving rise to powder deposits [5–13].

Plasma polymerization mechanisms can be distinguished by the type of monomer used in the polymerization process. If the monomer is unsaturated, the plasma may induce polymerization by creating reactive species in the electrical discharge, and the molecular weight then increases by a more conventional step-growth fashion. The quantity of aliphatic components that led to a hydrocarbon-type polymer with significant unsaturation and crosslinking verified that extensive modification of the initial monomer occurred. The chains were short and branched, and randomly terminated with frequent crosslinks. The network had no repeating units and contained a number of various functional groups [4].

Two types of polymerization processes may occur during plasma processes, plasma induced polymerization and plasma-state polymerization. Plasma-induced polymerizations occur only with unsaturated monomers and are essentially step-growth polymerizations initiated by the reactive species contained in the plasma. Plasma-state polymerizations are atomic processes that can only occur in a plasma and produce non-polymer-forming byproducts. [13]

The chosen monomer presents a structure able to form the network, which will be capable to keep the biologically active molecule (Fig. 2). There is already known the multitude possibilities of utilising polystyrene and poly(methyl methacrylate) in biomedical fields, such as: petri boxes, hemolysis tubes, connection elements for catheters and syringe bodies, matrices for bioactive composite, contact lenses).

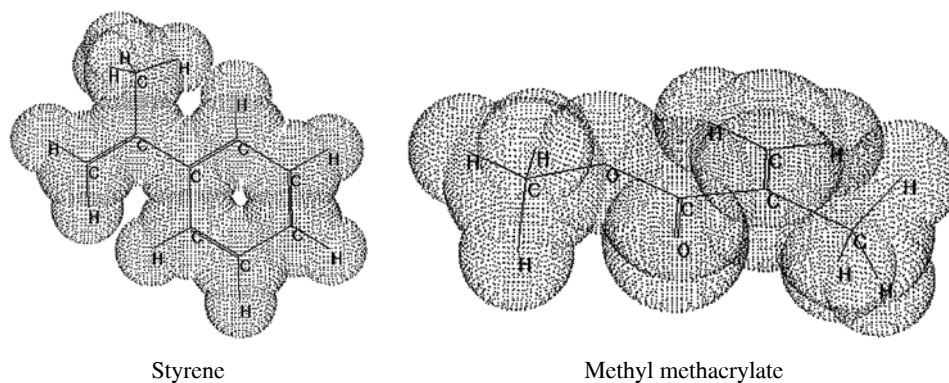


Fig. 2. – The monomer structure.

The FTIR spectra evidenced the plasma influence concretized through the decrease of adsorption bands intensity of the polymers, with the increasing of reaction time (Fig. 3). This aspect is explained through the cross-linking effect of plasma which determinate the increase of the interaction in the macromolecular chains.

The occurred modifications in **FTIR** spectra as a consequence of plasma action, explained by the molecular structure and by the interactions between them

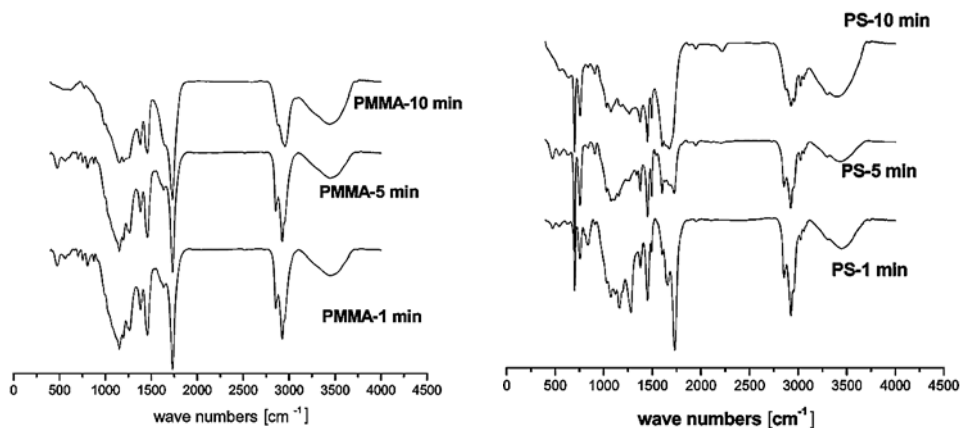


Fig. 3. – FTIR spectra of polymer structure synthesised in plasma at different reaction time.

them, are proved by a decrease of the absorption' intensity of the vibrations, as well as by changing of the peak's aspect.

Thus, it can be observed that the aspect of  $\nu\text{CH}_2$  characteristic bands for polystyrene from 2925 and 2850  $\text{cm}^{-1}$ , respectively the  $\text{O}(\text{CH}_3)$  characteristic bands for poly(methyl methacrylate) from 2920 and 2844  $\text{cm}^{-1}$  is changed, probably because of the cross-linking appearance (Fig. 4). The appearance of cross-linked bridges is also confirmed by the test of solubility. The plasma synthesized polymers are not soluble in their usual solvents: acetone, benzene, chloroform, etc.

However, both vinyl compounds are not destroyed in plasma polymerization. That is evidenced in FTIR spectra (Figs. 3–5).

The obtained macromolecular structure by plasma polymerization was also characterized by SEM technique. This method of investigation shows the formation of a network with cross-linked bridges (Fig. 6) for both homopolymers

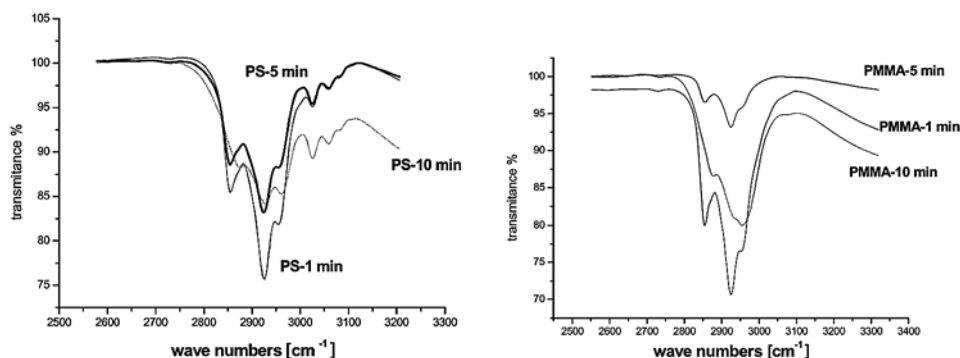


Fig. 4. – The evidence of the changes in the characteristic band profile.

PMMA and PSt. It is also remarked for the swelled sample the appearance of the network as being of a semi-interpenetrated type (Fig. 6 b, d). Both the swelled and dried structures present an order of the chains. At the same time, the dried samples present a fibrillar structure unusually for the amorphous polymer. This aspect is explained through the plasma effect that induces the increased number of the crosslinked bridges during the polymerization time.

#### 4. CONCLUSIONS

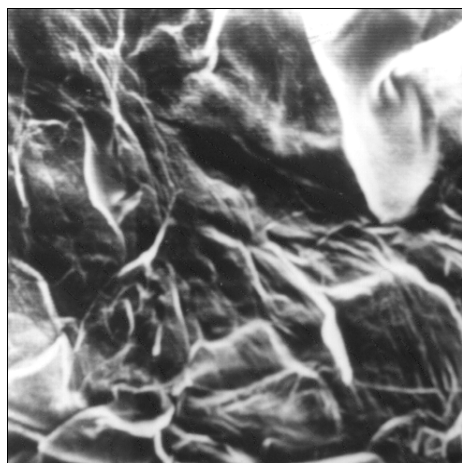
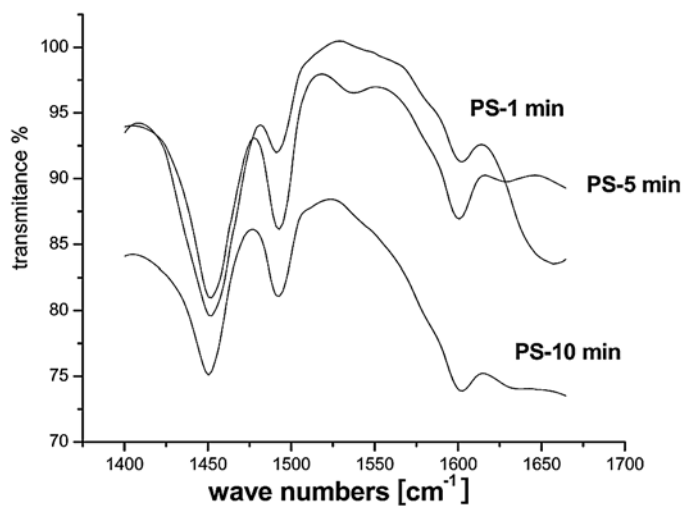
The use of plasma for polymer synthesis provides a basis in the future research endeavors for a number of interesting applications.

In this paper we are proposing the obtaining by plasma polymerization of a polymeric network structure based on styrene or methyl methacrylate. The aim of the synthesized networks is their use for subsequent coupling with a biological active compound. The realized macromolecular architecture can be applied as controlled release systems. The network structure of the synthesized matrices was evidenced by SEM technique, polymers being also characterized from the structural point of view through FTIR spectra.

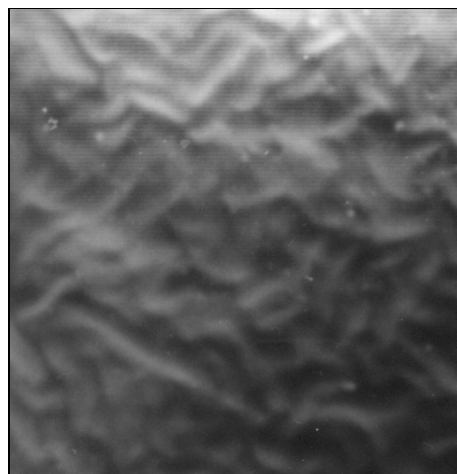
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Fig. 5. – The integrity maintaining of the benzene ring characteristic bands after the plasma treatment.



a



b



c



d

Fig. 6. – The SEM microscopy for the sample which are polymerized 10 min time: a) PMMA dry ( $\times 281$ ), b) PMMA-swelling ( $\times 848$ ), c) PS-dry ( $\times 196$ ), d) PS-swelling ( $\times 848$ ).