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ORIGINAL PAPER

Biomimethics effects during formation of membranes

Mariana BEZDADEA, Militina BOURCEANU
Technical University "Gh. Asachi" of Iasi, Faculty of Chemical Engineering, Dep. of Biochemical Engineering, 71 D. Mangeron Avenue, 700050 Iasi, Romania, email: mabedanmembran@yahoo.com

Abstract

The paper evidences the role played by the nature of the chemical links established in the development of supramolecular structures. Certain aspects of matrix polymerization and of the development of membrane structures during processing are discussed with special reference to the "hosts" capable of establishing links with the "guest" molecules.

The polymer-polymer interactions formed in the supramolecular structures, i.e. matrix compounds or "host-guest", or "replica" (template) compounds, bring into attention some important biological functions respectively, tailor membranes. The membranes obtains by this way are very largest applications in pharmaceutical, food chemistry and technical medical fields.

Introduction

The reactions leading to the obtaining of some chemical species which exhibit at least one structural or configurational property due to the matrix are generally referred to as matrix reactions.

Far for being limited to the reaction initiation the matrix or template and/or replica, also influences the whole process, that in the growing reaction in case of polymerization, or of the development of the membrane structure during the polymer processing. In this connection the choose of an adequate matrix host is particularly significant [1,2-14].

The orientation in the "host" matrix of polymer "guest" or bringing of the "guest" monomers in the most favourable position for the reaction, to obtain a new molecule or macromolecule, or polymer blend, is accomplished by means of hydrogen bonds, electrostatic attraction, covalent bonds, Van der Waals forces.

When classifying the "hosts" well defined groups or type only have to be considered. A unitary point of departure could be the type of chemical bond created during the interaction between "host" and "guest" molecules. In case of matrix polymerization or of development of the membrane structure during the polymer processing a simultaneous manifestation of intra and intermolecular effects is to be expected. A classification of the known "hosts" is listed in Table 1.

Table 1. Classification of molecules or macromolecules used as "hosts" in the polymerization reactions and the type of bonds settled with the "guest" molecules[2]

Nr.	Bond type	Host
1.	Covalent-bonds	- condensation products of p-cresol with methanol, cellulose with polystyrene-chlor-acetyl
2.	Electrostatic attraction	- poly (L-lysine), poly (styrene-sulphonic) acids, poly (ethylene-sulphonic) acids, poly(4-vinyl-pyridine), poly(2-vinyl-pyridine), $CdCl_2$, polystyrene-chlor-acetyl with 4,4` dipiridil
3.	Van der Waals forces	**-** iodine, urea and thiourea, perhydrotriphenylene, montmorillonite polyethylene oxide, poly (benzofuran), aluminum oxide, poly(N-vinylpyrrolidone), capronic fibers, polymethylmetacrylate, poly(tetrafluor-ethylene), acetate cellulose fibers.
4.	Hydrogen bonds	Hydroquinone, cyclodextrin, tri-o-thimotide, methyl-cellulose, chitin, cis-cyclo-butan-dimethyl-dicarboxilic-1,3 acid, poly (methylmetacrylate), deoxycholic acid (DCA), Sephadex, zeolite, water, starch, cellulose, acetate cellulose fibers.

The present paper mentions some methods of supramolecular architectural organization with formation of semi-permeable membranes.

Two original procedures have been applied, as follows:

- "host-guest" polymerization or matrix and/or "template" (replica) polymerization (polyvinylacetate membrane);

- development of the membrane structures during the polymer processing (polyurethane membrane, polystyrene membrane).

Cellulose, starch, sepfadex, zeolites, urea, water, cellulose fibers have been utilized as hosts or matrix (replica or template).

If in 1956, Lathe and Ruthren, the pioneers of experiments with columns of granular starch intended for filtration, offered an operation of chromatographical separation through which the solute, "molecules" were with held during their passing through the fixed bed in decreasing succession, regarding their size, their dimensions, making possible to estimate the molecule size and the molecular weight, five years later, Granath and Flodin, in 1961 introduce a porous medium superior to the starch granules: Sephadex. But the starch columns or Sephadex, could be replaced with matrix polymeric films of poly(vinylacetat) and utilized for separation and concentration of biosynthesis products (Penicillin G, proteins, amino acids) [6-8,14]

Materials and method

Materials

Membranes from polyurethane (PU), polyurethane modified with the following glycidyls: epichlorhydrin (ECH), phenylglycidylether (PhGE), β naphthylglycidylether (β NGE), polystyrene (PS), polystyrene modified with 4,4`- dipiridil, have been prepared by the

development of membrane structure during the polymer processing has been achieved [2,9,14] (development of the membrane structures during the polymer working).

Membranes from poly(vinylacetate) (PVAc) have been prepared by matrix method [2,3-8,10-12].

Method

The miscibility of the derivative polyurethane system, has been characterized by scanning electronic microscopy (SEM) with a Leitz-Rem 1600T electron microscope [14]. SEM image of PVAc sample synthesized by matrix polymerization was performed with the aid of a Phillips 400 electron microscope [6-8].

The matrix photo-polymerization of VAc was accomplished in quartz ampoules with 3 cm. inner diameter and provided with cooling coils, using an inert medium and UV emitted by a mercury lamp (500W). Sephadex, starch, zeolite, water, urea, was used as matrix. The resistant film, which can conserve his shape and elasticity in water, is obtained from the reactor polymerization of VAC. This film has a regulated microstructure and superiors physical-mechanical coefficients.

The miscibility of the derivative polystyrene system has been characterized by scanning electronic microscopy(Tesla BS 300 electron microscope: $U = 20kV$, $\alpha = 60^0$)
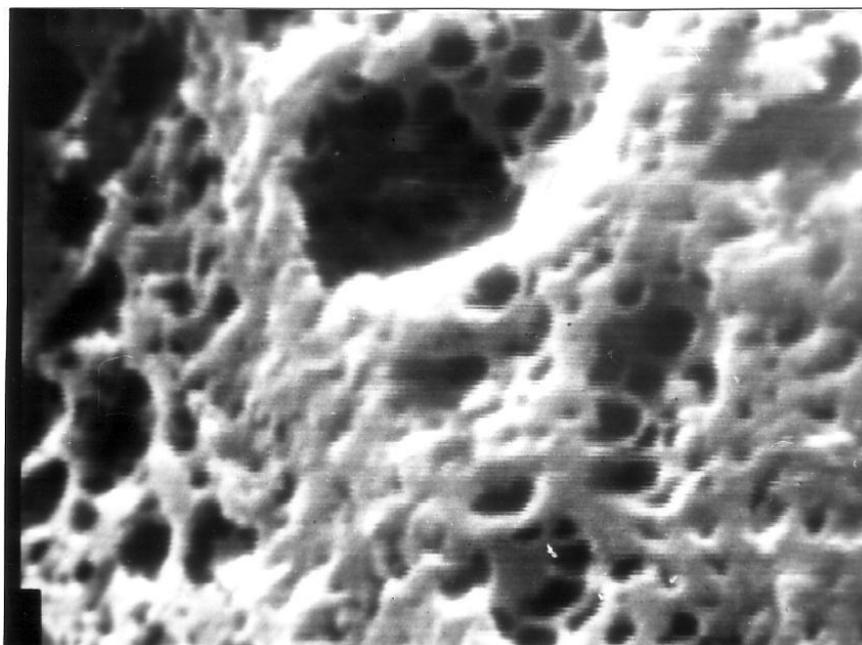

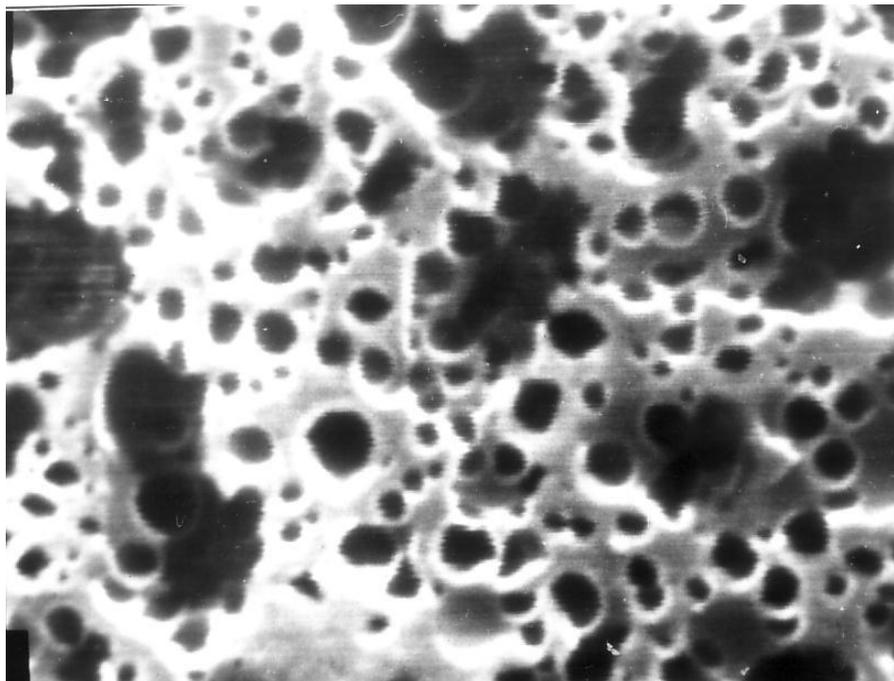**Figure 1.a** SEM micrograph of the polystyrene membrane with 4,4`-dipyrydil

Figure 1.b. SEM micrograph of the polystyrene membrane without 4,4ˋ-dipyrydil

The miscibility of the derivative polyurethane system [14] and of the derivative poly(vinylacetate) system, has been characterized by IR spectroscopy. For infrared measurement a Specord-71 IR Karl Zeiss Yena spectrometer was used.

Replicate polymerization of the vinyl acetate shows the clear differentiations in the infrared spectrum by comparison with the atactic conventional polymer (Fig.2a)

For the matrix poly(vinylacetate), the band from 1090 cm^{-1} is to be distinguished, associated to an ordinate structure in accordance to the literature (Fig.2b)
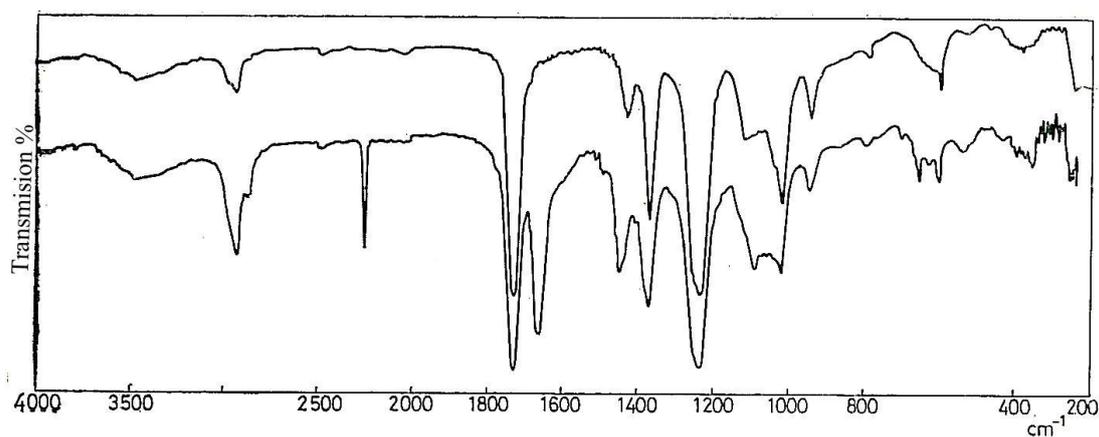

Figure 2.a. The infrared spectra of the atactic conventional PVac (1) and of matrix PVac (2)
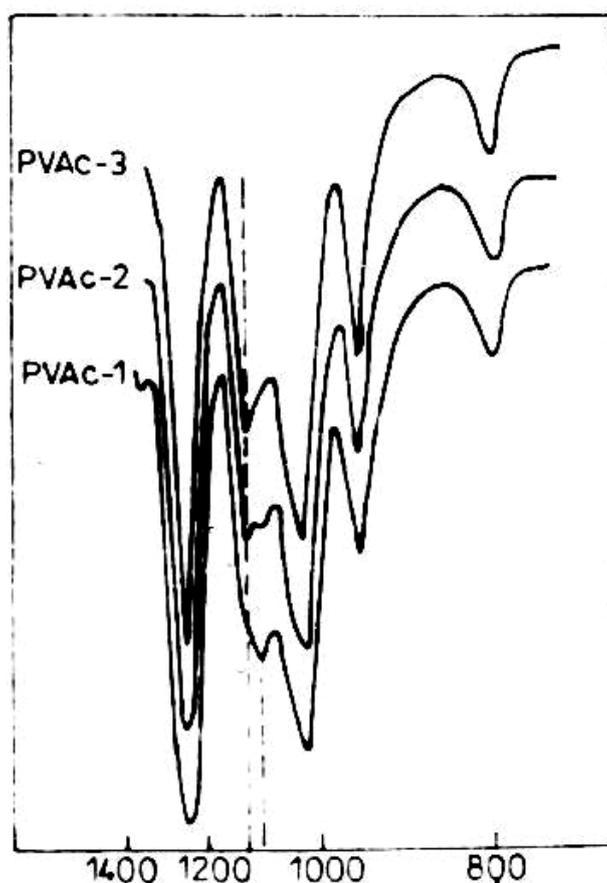
Figure 2.b The infrared spectra of PVAc in accordance to the literature:
PVAc-1 isotactic, PVAc-2 sindiotactic, PVAc-3 atactic

Results and discussion

Thus we obtain supramolecular architectural organization. The types of links "host-guest" are given as follows:

1. Covalent bond

There are of series of oligomers meeting this requirement. The condensation products of p-cresol and methanal (constituted of p-cresol structural units bound by methylene links) unitary from the molecular and structural point of view, easily obtainable for n = 2-10 are the most adequate compounds.

The reaction sequence (the attachment of acryl or metacrylester to a phenol molecule, the linking of esters to cyclooligomers, the hydrolytic splitting into the unitary oligoacrylic acids and the free phenol molecule) remainds of the model of protein biosynthesis [13].
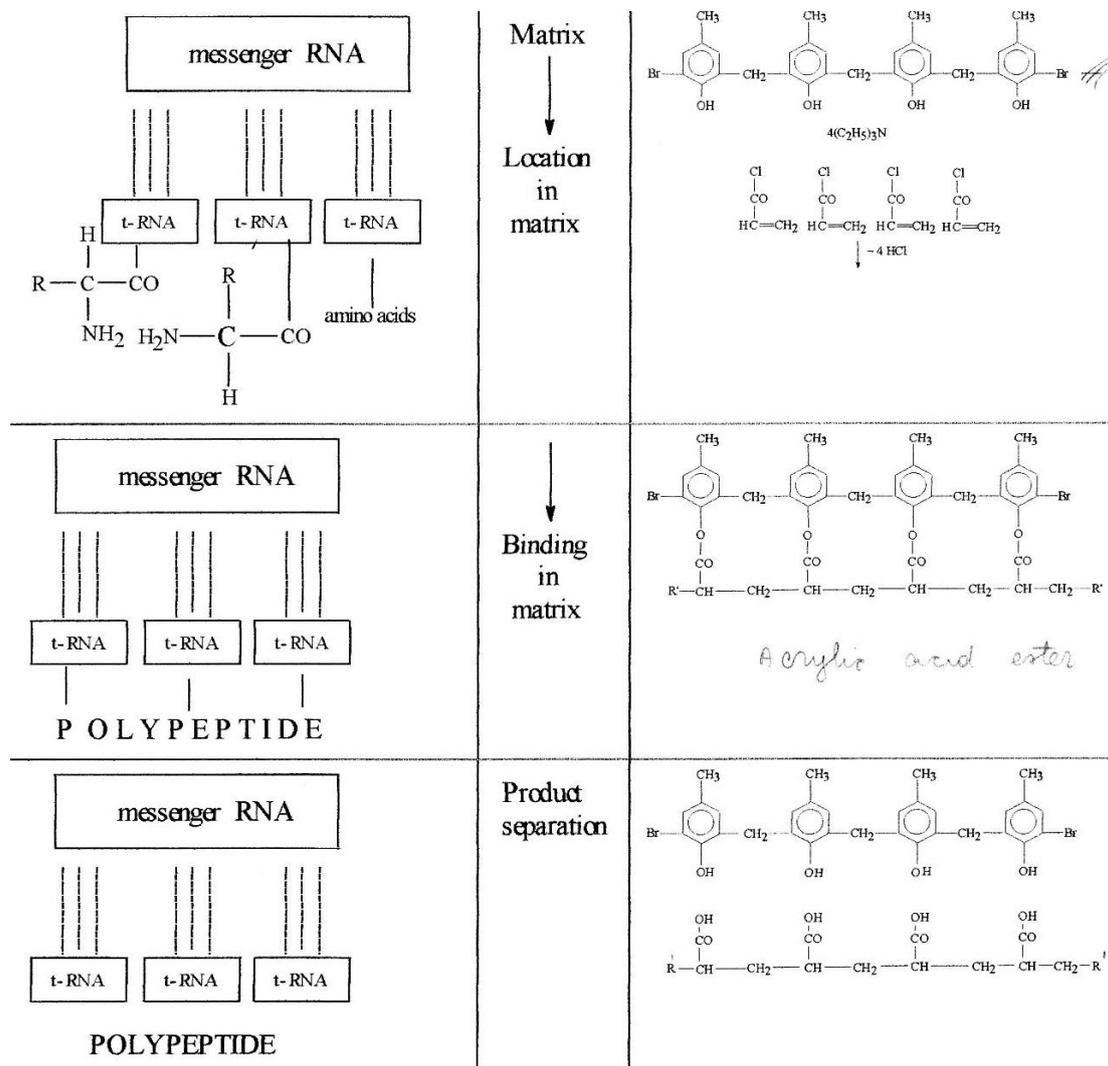
The polymer-polymer interactions formed in the supramolecular structures i.e. matrix compounds or "host-guest", or "replica" (template) compounds bring into attention semi-permeable membranes. Also, the cellulose "host" imparts to the polystyrene-chloracetyl "guest", attached to it by polymer working with covalent coordinative bond, the unitary character structure (membrane):
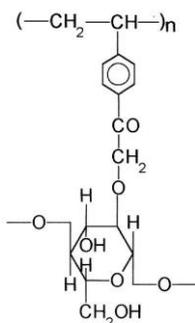
By using the glycidyls for obtaining polyurethane membranes significant structural changes have been recorded. Taking into account the reactivity of oxirane groups in glycidyls, the addition of these to the nitrogen atoms is possible, with the formation of branches and the partial destruction of the hydrogen bond associations [14] :
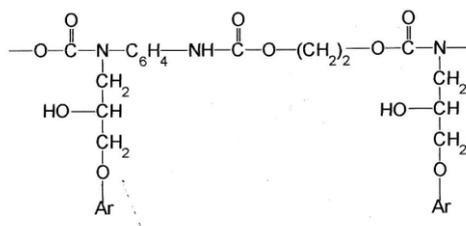

2. Electrostatic attraction

The cellulose "host" imparts to the polystyrene chloracetyl "guest" attached to it by polymer working and by 4,4` dipyrydil with covalent- coordinative bond, the membrane structure :
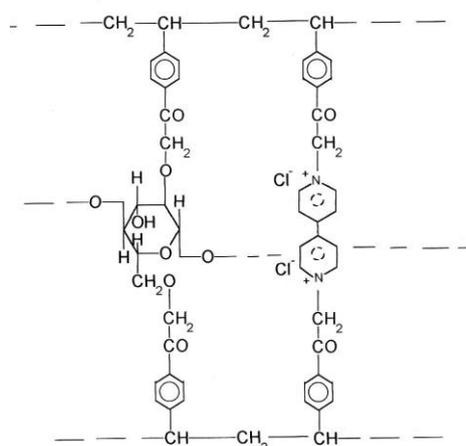

In matrix polymerization the intra and intermolecular effects in the chemical activation of monomers manifest simultaneously, various type of chemical linkages between host and guest being settled. Due to the electrostatic bonds the matrix reaction can be regarded as a particular case of the living polymerization. This is the case of polymerization of 4-vinyl-pyridine (4-VP) and of 2-vinyl-pyridine (2-VP), respectively [15].

By following the chemical action of 4-VP, through an intra-molecular effect in the reaction with an alkyl halide, carried out in an organic solvent (DMSO, benzene, methanol) at -5^0C, the macromolecules of the type given below, can be found:
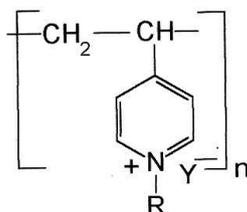

It was demonstrated that in the presence of low molecular anions (Cl^-, Br^-, CH_3COO^-, ClO_4^-, SO_4^{2-}), the rate of living polymerization of 4-VP is much slower than that in the presence of organic polyanions, such as the poly (styrene sulphonic) acid (PSSA).

Thus, by polymerizing 4-VP on PSSA a compound of the form given below is obtained [16].
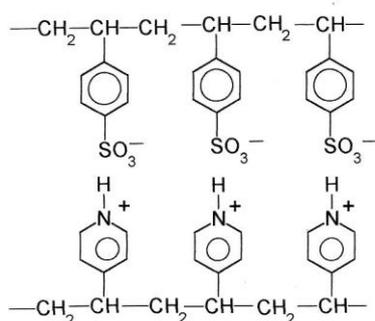
An electrostatic attachment of 4-vinylpyridine to polyanions is noticed, the monomer polymerizing in the anionic matrix.

Allan and Fontanille evidenced the stereospecific anionic living polymerization of 2-PV; the degree of isotacticity of the polymer in benzen is of 0,9. The development of living chain is specified by the complexation of Mg cation with last and with the last but one pyridine rings of the living polymer chain. When using benzyl-2-pyridine methyl magnesium (B/Mg/Py) as initiator, in the polymerization only a type of carbanionic species in encountered $BzMg^+$ being the cation [15].
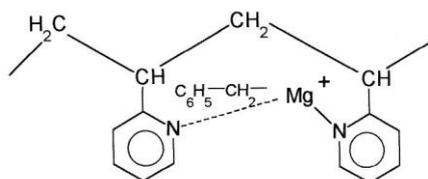
1-4 disubstituted butadienes, with R-CH=CH-CH=CH-CH$_2$NH$_2$ with R = H, CH$_3$, COOH, and COOR may polymerize through UV irradiation or high energy radiation in an inorganic matrix of CdCl$_2$. Apart from the host, after precipitation of the Cd ions in the CdS form, the stereoregular polymer obtained behaves like an ampholite. The structural analysis evidences the formation of a stereoregular 1,4-trans-polybutadienic chain, through an 1,4-addition mechanism **(Fig. 3).**
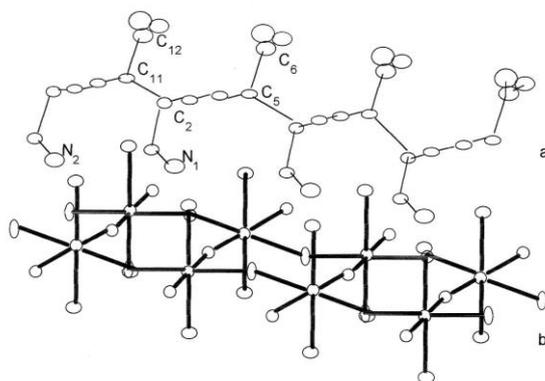
Figure 3. General view of the inorganic and polymeric network:
a) polymeric network; b) network of the inorganic host.

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Formation of a complex between the polymer and the Cd ions may be assumed, so that both compounds are already contained in the crystals in a 2:1 stoichiometric ration. The polymer's "zwitterion" type structure is:
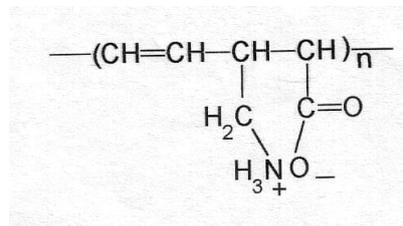

3. Van der Waals links

Solid-state polymerization of diacetylenes represents a first example of a controlled, solid-state matrix reaction. It represents a typical example of self-catalysis, which involves the formation of the macromolecular chain in the monomer's crystalline network. The polymer's stereoregularity has a strong effect on the physical and mechanical properties. The scale-type cyclic polymer obtained through solide-state polymerization of cyclic-tetramer has a considerable mechanical strength[18] :
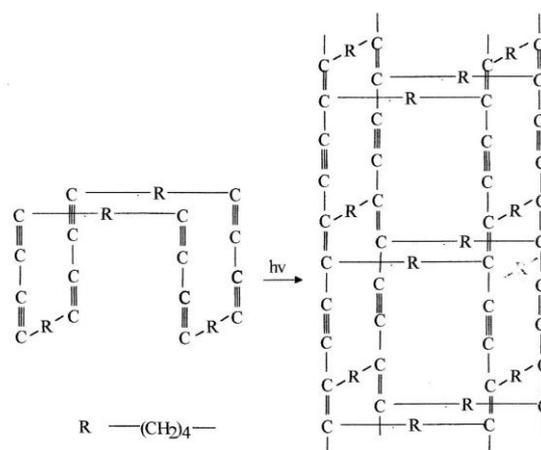
The matrix effects put into evidence through the polymerization of acrylonitrile in the presence of the pre-formed polymer, show a self -acceleration character for the reaction of polymer formation, characterized by a low value of the activation energy[19].
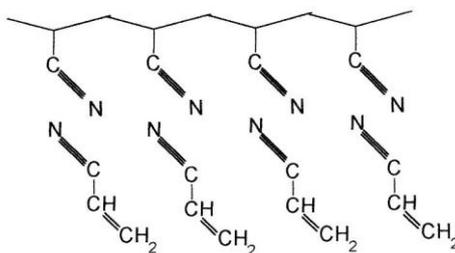
De Paoli, Tamashita and Galembeck [20] studied photochemical polymerization of vinyl-acetate (VAc) adsorbed on the polytetrafluorethylene (PTFE) matrix, thus evidencing the process developed both on the PTFE surface and within its mass. The IR spectrum of the vinyl acetate sorbed in PTFE evidences peaks at 2960 cm^{-1} (ν_{CH}), 1780 cm^{-1} ($\nu_{C=O}$), 1660 cm^{-1} ($\nu_{C=C}$) and shoulders at 1410 cm^{-1} and 1380 cm^{-1} (ν_{CH3}).

The bands, are modified at frequencies higher with about 20 cm^{-1}, through adsorption in PTFE, indicating for the adsorbed molecules a special behaviour, explainable by the matrix presence.

The importance of these matrix techniques, applied on PTFE, lies not only in the production of some new composite materials, but also improves knowledge on the photochemical processes occurring between the cellular membranes which may be therefore employed as a model for photobiological systems.
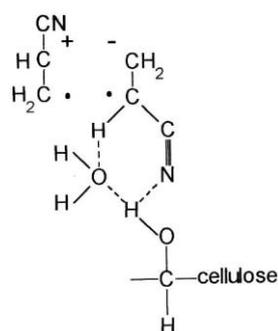
4. Hydrogen bond

The hosts-guest" interactions through hydrogen bridges are of real interest since they play a significant role in nucleic acids and proteins and cooperate in biological synthesis by orienting the structural units prior to the bond formation.

The following groups of "hosts" (matrix or replica) involve hydrogen bonds:
a) canal type (tunnel) "hosts"
- deoxycholic acid (DCA)
- tri-o-thymotide
- 4,4ˈ dihydroxytriphenilmethane
- sephadex
- zeolites
b) Cavity (cage) "hosts"
- cyclodextrin
- water
- zeolites
c) replicate matrix
- poly (carboxylic acids)
- cellulose
- starch
- Sephadex

The polysaccharides, the methyl-cellulose, the starch, sephadex are included among the compounds which can serve as orienting surface in the template polymerization (hydrogen links) or in the development of the membrane structure during the polymer processing. They can serve as hosts due to the ability of their surface to orient the guest. In other words they facilitate a specific adsorption unlike the common adsorption offered by alumina or silica gel [2,6-8,21,22].

Gaylord [23] assigned to cellulose a complexing action by which the monomers are activated and at the same time a matrix role for aligning the complexes of the formed acceptor monomers (A^+….A^- cellulose-water) and donor-acceptor (D^+….A^- -cellulose-water). Hence, the initiation is assumed to take place by with drawing a proton from the monomer, included in the acceptor-donor complex, by the radicals found in the system. The synthesized macromolecular chain can be grafted on the support polymer or can remain detached as homopolymer. For instance, for the cellulose-water-acrylonitrile the following structure is given below:

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The –OH groups of dextrin play both the electron –donating and electron-with drawing role, forming hydrogen bonds with the "guest" molecules. There is a attraction-repulsion mechanism and this stereochemistry of the host-guest attack reminds of the "lock and key" mechanism suggested by Fischer for the enzymatic catalysis [6-8]. The catalytic role of cyclodextrins mentioned by Cramer [24] for the stereo specific reactions of decarboxylation and phosphorylation, as well as the advanced mechanism, is analogous to that advanced by Imoto [1] in 1967, for the polymerization of methyl methacrylate (MAM) in the presence of water and polyvinylalcohol (PVA) oligomer which proceeds according to a radicalic mechanism:
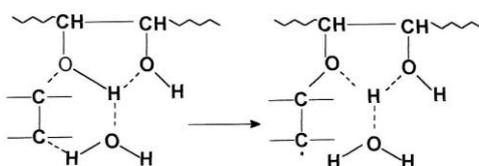

Separately, Kimura and co-wokers [25] investigated the polymerization of the ethyl-acrylate with starch and water, and Bezdadea M.[2] followed as hosts molecules the following substances have been used: sephadex, starch, cellulose-acetate, zeolite and water for two methods of supramolecular architectural organization with formation of polyvinyl acetate and polyurethane membranes:
   - host-guest polymerization or matrix and/or template and/or replica [6-8].
   - Development of the membrane structures during the polymer processing[14].
   For the polysaccharides-water-vinylacetate (a) and polyurethane-cellulose (b) the following structures is:

a

b
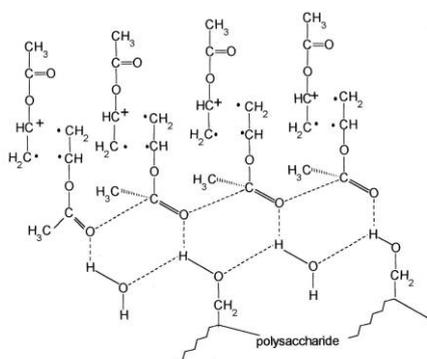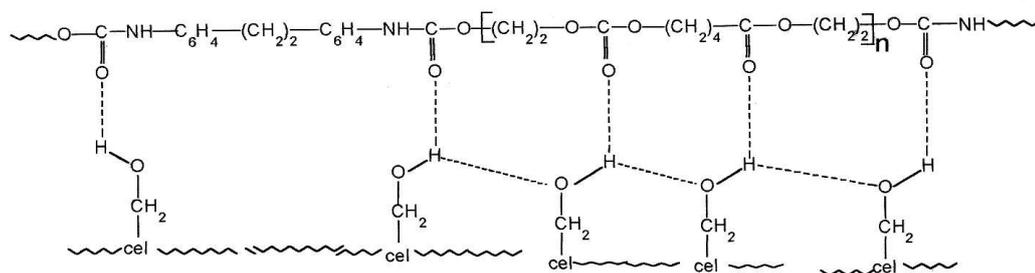
Zeolites, as well as most biological systems, contain sites of a certain polarity or charge, and also water, in a certain structured state, somewhere between that of ice and of liquid water[8,26].

Conclusions

1. An interesting analogy of the techniques of membrane organization, and the specific character of those met in biological systems is put into evidence.

2. Such techniques lead to supramolecular architectures that may provide data on the photochemical processes occurring between the cellular membranes.

3. The supramolecular structures are similar with the organized compounds having specific properties, of the type of functional membranes from living organisms.

4. Two original procedures have been applied as follows:

- Host-guest polymerization or matrix polymerization (PVAc membrane) and

- Development of the membrane structures during the polymer processing (PU membrane and PS membrane)

5. More recently membrane developers are increasingly using tailor-made polymers [27].

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