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Characterization of poly(2-hydroxyethyl methacrylate) (PHEMA) contact lens using the Langmuir monolayer technique

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ABSTRACT

The behavior of poly(2-hydroxyethyl methacrylate) (PHEMA) polymer monolayer spread on water was studied under various experimental conditions. The influence of subphase pH and temperature, compression speed, elapsed time from the deposit of the monolayer and the recording of the surface pressure–area (π–A) isotherms, as well as the number of polymer molecules deposited at the air/water surface (surface concentration) was studied. The obtained results show that PHEMA exhibits a very stable monolayer given that it is unaffected by modifications in the majority of these variables. Only the elapsed time between the spreading of the monolayer and the beginning of compression causes a small change in the π–A isotherms that consists in an increase in the area occupied by the film. This is attributed to the greater unfolding with time of the polymer's monomers at the air/water interface.

The plateau that appears on π–A curves of the PHEMA monolayer is attributed to the reorientation of their hydroxyethyl polar groups through their C–O–C bonds, as well as to the reorientation of the ethylene (CH_2) groups that link the monomers, which provokes a folding of the polymer's chains causing an *accordion* configuration. The existence of this structure is confirmed by the presence of numerous noise peaks in the relative thickness versus time curve corresponding to this region. In the same fashion, the images observed from Brewster angle microscopy (BAM) reveal the existence of light–dark "bands" relative to the different regions of this particular structure.

1. Introduction

PHEMA is a transparent hydrogel, biocompatible, with good mechanical and stability properties, which makes it especially suitable for the manufacture of contact lenses or medical delivery systems. It was synthesized by Wichterle and Lim [1] with the purpose of developing soft contact lenses with greater oxygen permeability and more comfortable than hard poly(methyl methacrylate) (PMMA) lenses used until then.

From a structural point of view, soft contact lenses are copolymers (Scheme 1) formed by acrylic polymers of 2-hydroxyethyl methacrylate (HEMA) and by linking agents (such as ethylene glycol dimethylacrylate, EGDMA) incorporated to the basis monomer to give rise the overlapping of the chains polymer in 3D networks with the goal to confer the adequate stability and mechanical rigidity that a contact lens requires, given that without the presence of these linking agents, the majority of the hydrophilic contact lenses would be water soluble.

The property most characteristic of these hydrogels is their intrinsic capacity to absorb water (up to 38%), which permits atmospheric oxygen dissolution when they come into contact with air. As such, gas diffusion is increased, and, as a result, the oxygen permeability problem is partially solved with respect to hard (hydrophobic) contact lenses, which are less physiological. Another advantage to keep in mind is that tear film is easily extended on hydrophilic PHEMA lenses due to its high surface tension. As a consequence of these properties, PHEMA soft contact lenses have displaced the older PMMA hard contact lenses in the market place, which, in turn, has contributed to the spectacular increase in the use of this kind of lens to correct refractive errors to the detriment of conventional glasses.

A problem that causes this type of lens is that their wettability decreases with use, owing to the fact that tear film lipids have a high affinity for PHEMA. This provokes their deposition on the contact lenses and, consequently, vision discomfort. Hence, the reason why further knowledge of how PHEMA interacts with the teardrop lipid components is fundamental in order to better understand the behavior of this polymer in the eye.

In addition, the use of PHEMA contact lenses as pharmaceutical delivery systems is gaining increasing attention due to the fact that their biocompatibility and user acceptance is completely documented and guaranteed. It is well known that when pharmaceutical drugs are administered into the eye, only a limited part of the dose

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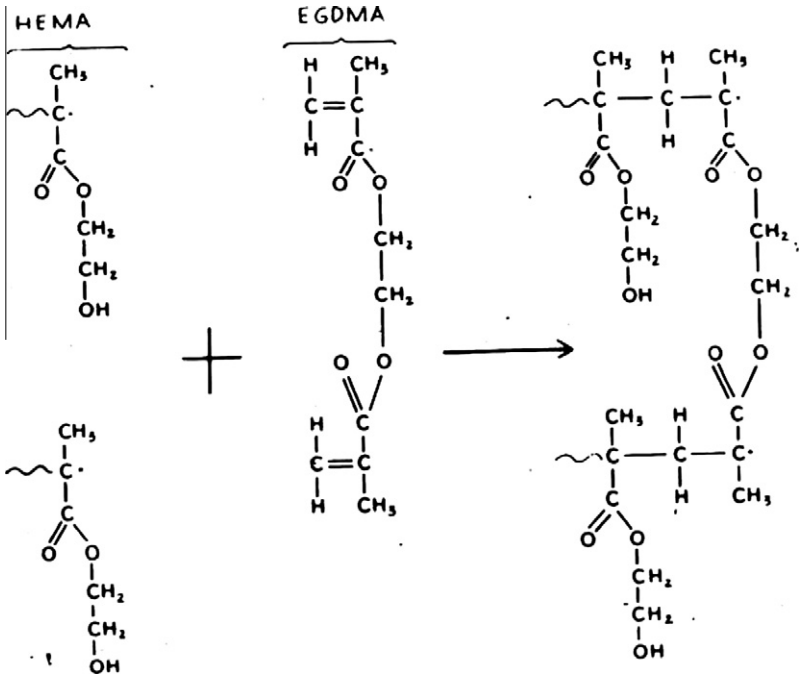

Scheme 1. Schematic chemical structure of soft PHEMA contact lens.

penetrates through the cornea to the aqueous humor, where its therapeutic effect takes place. The remaining part of the dose is swept by tear fluid through the nasolachrymal conduct towards the digestive apparatus or is unproductively absorbed through the conjunctiva. In addition, teardrop secretion and blinking of the eye provokes an intensive drainage effect, which is such that when eye-drops are administered in the eye their velocity of the elimination from the precorneal area is more than 100 times the velocity with which it penetrates through the cornea. This suggests that less than 1% of the applied dose reaches the internal structure of the eye. Thus, application has to be frequently repeated if the desired effective concentrations at the structural ocular levels are to be achieved. This is why the use of therapeutic contact lenses (TCLs) as pharmaceutical drug delivery devices has been awakening ever greater interest in recent years, given that they could constitute an important therapeutic alternative at the ocular level going beyond the correction of ametropia problems, for example, in the treatment of glaucoma and infectious or inflammatory processes, in post-traumatic or post-operative medical administration, in the treatment of dry eye or treating allergic reactions, and in vascular alterations and degenerative processes of the ocular system [2–7].

With this in mind, the aim of this work is to characterize the surface behavior of PHEMA by means of the Langmuir monolayer technique with the goal of later studying the interaction of this hydrogel with different components of the tear film, as well as with pharmaceutical drugs that could be administered via therapeutic contact lenses. Since PHEMA has not been previously characterized using the monolayer technique, in this work a study of the various factors that affect optimal spreading, necessary to achieve reproducible PHEMA monolayers at the air/water interface, was carried out. To achieve this end, we studied the influence of the number of polymer molecules spread at the air/water interface, the elapsed time between the polymer's deposit and the start of the monolayer compression, the compression speed, the temperature and the subphase pH, as well as the behavior of the monolayer when subjected to successive compression-decompression cycles. Lastly, the morphological characteristics and relative thickness of the monolayer were likewise studied using the Brewster angle microscopy technique (BAM).

To summarize, the knowledge of the PHEMA monolayer's behavior under different experimental conditions is an indispensable prerequisite for the subsequent study of mixed monolayers consisting of this polymer and the distinct teardrop components, on the one hand, as well as the various pharmaceuticals drugs subject to ocular administration via the utilization of PHEMA lenses, on the other hand.

2. Experimental methods

2.1. Materials

PHEMA was supplied by Polysciences Inc. as a solution with 12% concentration in ethanol. For the monolayer formation a spreading solution with 0.6 mg/ml PHEMA concentration was used. A few drops of *n*-amyl alcohol (Merck-Schuchardt) were added to this spreading solution to facilitate its extension at the *A*/*W* interface. Adequate volumes of this spreading solution were spread to attain, in most cases, an initial number of polymer molecules of 1.7×10^{14}, which corresponds to a value of 2.6×10^{17} monomers. For these calculations an average polymer molecular weight of 200,000 g/mol (1537 monomers) (data supplied by Polysciences Inc.), was used. The polydispersity was not measured since, according to other authors [8–11], the molecular weight distribution effect is believed to be minimal on the monolayer behavior.

Ultrapure water used as subphase was obtained from a Milli-Ro, Milli-Q reverse osmosis system (Millipore Corp.), with a resistivity of 18.2 MΩ cm. Regulation of the trough temperature was controlled by circulating constant temperature water from a Haake thermostat through the tubes attached to the aluminum-based plate of the trough. The subphase temperature was measured by a thermocouple located just below the air/water interface.

2.2. Surface trough

To observe the morphological characteristics of PHEMA monolayers by Brewster angle microscopy (BAM), experiments were carried out with a Nima 601 trough (Coventry, UK) placed on a anti-