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Role and Significance of Residual Monomer MMA for the Comfort of Patients Using PMA Contact Lenses

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Abstract

This article describes HSGS method for determination of Methylmethacrylate (MMA) in polymeric matrixes of Polymethylmetacrylate (PMMA) in rigid contact lenses for correction of refractive errors. The non-polymerized MMA has to be kept under certain values determined by specific regulations because it can restrict oxygen diffusion through the contact lens and cause ocular complications such as hypoxia and corneal oedema.

Keywords: Rigid contact lenses RGP; front eye surface; complications; Methylmethacrylate; Headspace (HSGC).

1. Introduction

Today 85% of the rigid contact lenses are made of polymethyl methacrylate, and another 10% are composed of its copolymers such as 1-vinyl-2-pyrrolidone, 2-hydroxyethyl methacrylate, silyl esters of methacrylic acid and others. 2% of the world's population wear contact lenses, 2/3 of which being women.

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Most contact lens users wear the so called soft lenses made of silicone hydrogels. They offer greater comfort but require specific maintenance and have shorter life. The rigid contact lenses, made primarily by PMMA, might got worn out but practically do not get old. Their maintenance is not complicated and their application in specific conditions, such as keratoconus and inappropriate astigmatism, is indispensable. For these reasons, despite the slight discomfort and the higher initial cost for the patient, they have a well-established position among the patients with contact correction. A major complaint from conducted surveys among RGP users is discomfort and feeling of a foreign body accompanying the patient throughout the day. This results from the geometry of the lens and its profile, as well as from the corneal hypoxia. It is caused by the proximity of the polymer chains as well as by the presence of unreacted monomer between them. The most typical phenomena are redness, epithelial oedema, stromal oedema and enlargement of the perilimbal vessels. The presence of an unreacted methyl methacrylate in the polymers used in the contact lenses influences both the optical properties of the lens and the tolerance from the body - the tendency to cause allergies [1,2,3]. The free monomer prevents diffusion of oxygen through the lens, which is one of the main indicators of the product's quality. Usually, manufacturers refrain from commenting on the relationship between the two indicators, but it is generally assumed that the free methyl methacrylate content should not exceed 3%.

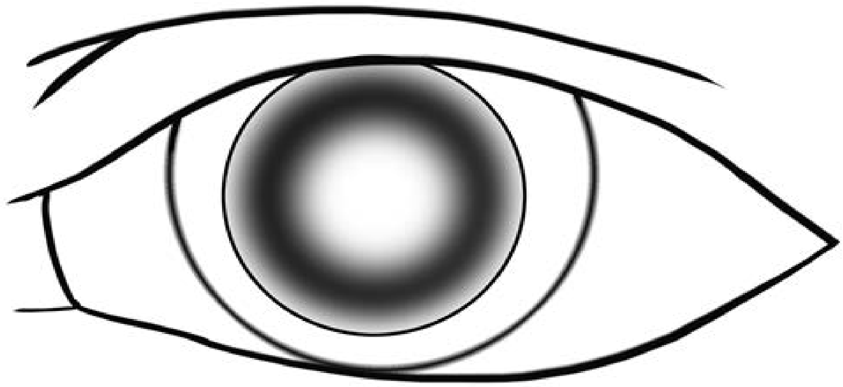

Figure1: RGP fitting in front

The question of the content of unreacted monomer is regulated by Directive 90/385 / EEC, Directive 93/42 / EEC and Directive 2007/47 [4,5,6]. It is specified that the free monomer content may not exceed 3% of the weight of the product. Other publications [7] examine the topic of free methyl methacrylate in contact lenses. In the author's work, a detailed control method using gas chromatography [8,9] is described. The competitive market conditions call for the promotion of products from different manufacturers, including local ones.

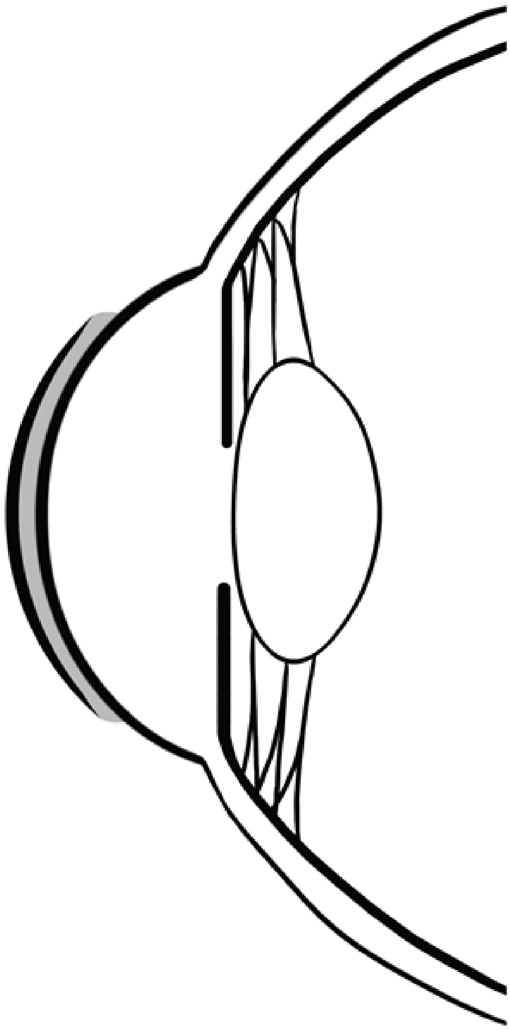

Figure 2: RGP fitting in profile

2. Experimental

In order to determine the content of unpolymerizied MMA in PMMA contact lenses, it is necessary to dissolve the polymer in a solvent with higher boiling point than MMA. To this end it is sufficient to weigh exactly a lens sample within the range 0,004-0,005g to 4 decimal places, it is than placed in a headspace vial, 2 ml DMF added and the vial top with Teflon coated septum is tightened. A 1mg cm-3 standard solution of MMA is prepared, in DMF – the monomer being freshly distilled. It is kept at 0*C.

Working standards of 50-100 ppm are prepared from it as per the operator’s choice consisting of 100-200mml standard solution and 1, 9-1, 8 ml DMF.

A series of standard additions of MMA to PMMA suspension is used to characterize the method. PMMA suspension is used in this case because it is practically monomer free in terms of the detection limit of the method.

A Perkin- Elmer HS-6 headspace unit attached to Sigma 1 gas chromatograph was used for the analysis. Samples were equilibrated for 15 min at 80*C in the headspace unit. In the gas chromatograph, a 2mh2mm glass column, packed with 10% Carbowax20M on Chromosorb WHP 80-100 mesh was used. Argon carrier gas was used at 200kPa. The temperature of the injector and detector were 150* and 200*C respectively. The oven temperature program was 3 min at 80*C, then 30*C and finally 4 min isothermal. After reducing the temperature to 80 *C, the unit was usually ready for use again in 15 min. An FID was used. The HS-6 unit temperature was 80*C. The proposed method of analyzing MMA in a rigid contact lens material is based on the dissolution of a part of the sample in DMF, which enables the equilibrium to draw to the MMA in the vapor phase and thereby leads to increase of the sensitivity. Under these conditions, the sensitivity is 1 mg / kg, and the variation factor is 3.8%. The gas chromatographic headspace method is characterized by the standard additive method in absolute external standard calibration.

Table 1: Reproducibility in determining the methyl methacrylate mg / dm3

No	Added quantity methyl methacrylate	Quantity found methyl methacrylate
1	25	24
2	25	25
3	25	26
4	50	48
5	50	52
6	50	48
7	50	50
8	100	96
9	100	104
10	100	100
	X	24,9
	SD	0,87
	RSD %	3,5%
	μ	24,9±0,6
	R^2	0,9964

The amount of unreacted monomer depends on the conditions of polymerization and the way it is initiated. 15 different types of polymeric materials for rigid contact lenses, most widely produced and used in Europe and in our country have been studied (Table II). They are dissolved in dimethylformamide. Similarly, the methyl methacrylate standard of 1 mg / ml has been prepared. The contact lenses have been delivered packaged as required by the manufacturer.

The studied contact lens materials have been obtained by various polymerization techniques. For comparison, a sample of suspension polymethylmethacrylate has been analyzed (No 5). It has a large and specific surface area and gets liberated from the monomeric residues by diffusion during the polymerization process. Each sample has been tested four times, the average values are shown in Table 2.

Table 2: Content of methyl methacrylate in material for rigid contact lenses

№	Type of material	N of peak (mm)	C mg/kg	%	Approx. weight g
1	Benzoyl peroxide initiator in excess	51	29	2,9	0,0047
2	Benzoyl peroxide equimolar	57	24	2,4	0,0062
3	Blowing with nitrogen	85	40	4,0	0,0056
4	Azo-bis-isobutyronitrile	128	59	5,9	0,0057
5	Suspended PMMA	-	-	-	0,0050
6	BASF No 1	-	-	-	0,0457
7	BASF No 2	17	1	0,1	0,0054
8	Lens X	-	-	-	0,0039
9	Bulgarian lens with azo-bis-isobutyronitrile	17	6,7	0,67	0,0067
10	Lens Button	82	36	3,6	0,0060
11	Bulgarian redox system	17	6,8	0,68	0,0063
12	Bausch & Lomb	19	1,1	0,11	0,0059
13	CIBA Vision Focus (Novartis)	14	0,8	0,08	0,0066
14	Johnson & Johnson	21	1,2	0,12	0,0061
15	Cooper Vision	18	0,9	0,09	0,0058
16	Vistacon	24	1,3	0,13	0,0064

The results show that not all samples correspond to the accepted norm of 3% for methyl methacrylate residue. Thus, the Bulgarian material for rigid contact lenses is adapted for use (No. 9) according to the above-mentioned requirements. As a whole, changes in the assortment of this type of medical product occur on the market over the course of time and now only positions 6 and 7 and from 12 to 16 as shown in the Table II below are present on the market, with the tendency for positions 6 and 7 to fall out gradually.

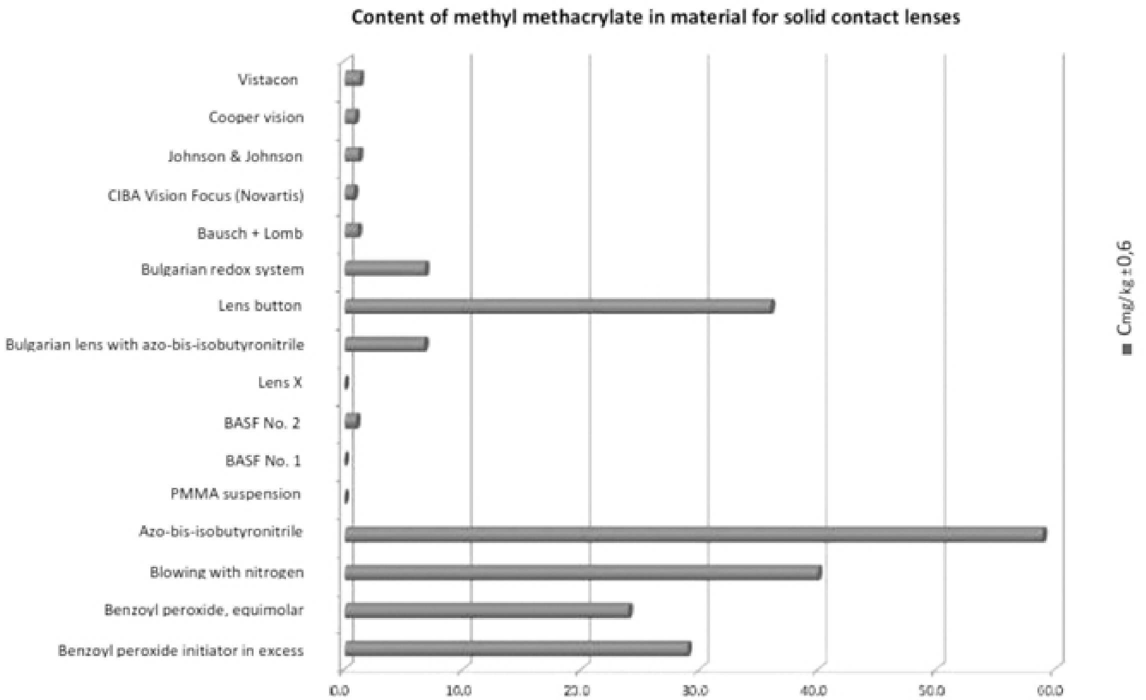

Figure 3: Graphic representation of Table II results for MMA content in PMA in rigid contact lenses

Figure 4 shows typical gas chromatograms for an external standard and unreacted MMA. They were obtained by examining two standards with a monomer of varying sensitivity, pure suspension polymer, and two examples of real medical products.

Figure 4: Standard chromatograms and samples of polymethyl methacrylate

1. MMA Standard with concentration 100 mg / dm3 at Attenuation 0
2. Defective contact lens with 3.13% MMA

U – unknown peak MMA - peak of methyl methacrylate DMF - dimethylformamide

3. Results and discussion

It is worthy to note that the content of unreacted monomer is significantly below the maximum allowed rate in the established lens nomenclatures as well as in their typical means for initiating the polymerization of MMA to PMMA. This suggests that manufacturers use standardized polymerization control to the maximum possible extent, as well as are prepared to reduce the content of the free monomer in case if WHO and EU regulatory changes.

This enables them to offer on the market a product with a maximum diffusion oxygen factor which reduces the potential complaints of the users. When the first 10 studied lens samples which reflect the experimental queries in the field of radical polymerization and its initiation are sorted and ranked according to the free MMA content, an interesting graph of the following type appears:

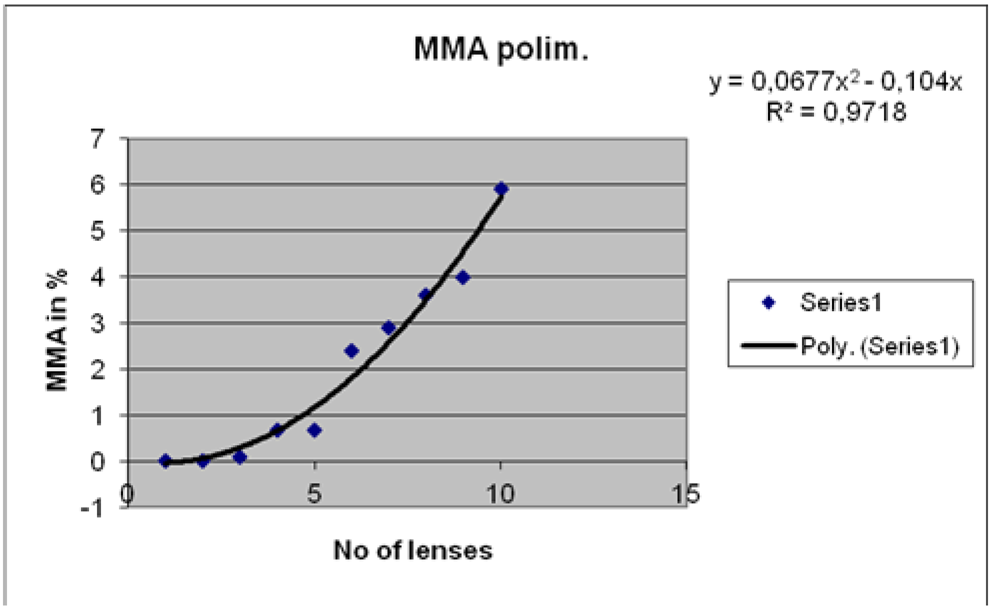

Figure 5: Dependence between the degree of polymerization and the amount of free monomer found in the polymer matrix

In the polynomial distribution, the equation y = 0.0677x2 -0.104x has a correlation R2 = 0.9718, which is a very good value. The graphics has a similarity to the kinetic curve of polymerization, despite the absence of time factor. From classical physical chemistry it is known that:

$\Delta F_{T,p}=\Delta H-T\Delta S$

where F- free Gibs energy, H-enthalpy, T- absolute Kelvin temperature, S- entropy

When $\Delta F=0$, it would mean $\Delta H= T\Delta S$.

When the partial pressure of the vapor is decreased at this temperature, the entropy rises, and

$T\Delta S> \Delta H$

$\Delta F<0$

Thus evaporation is spontaneous. If the partial pressure of the vapor is increased, the entropy falls, and

$T\Delta S<\Delta H$

$\Delta F>0$

In the polymerization of MMA to PMMA, T = 437 0K (164 ° C), there are temperature constraints for conducting the process, ΔH = -13.2, ΔS=-28, ΔF=-4,8, when T=298 ^{0}K for standard conditions. This indirectly indicates that in the process controlled by k2 - the equilibrium polymerization constant and k1 - the equilibrium depolymerization constant, they are determined by the temperature range 437-298 ° C. The ratio k2 / k1 = K is the equilibrium process constant, which in this case reaches 3.5.104. Hence, it is apparent that the process is entirely subordinate to van't Hoff's law, according to which the higher the temperature, the greater the concentration of vapor at equillibrium.

$\log \frac{k2}{k1} = \frac{Ea}{4.576}\left(\frac{1}{T1} - \frac{1}{T2}\right)$, where

k_2 – the equilibrium polymerization constant

k1 - the equilibrium depolymerization constant

E_a – energy of activation

T_1 - initial temperature

T_2 - end temperature

The van't Hoff equation can also be represented in the form

$\log \frac{K2}{K1} = \frac{\overline{(\Delta H)}}{4.576}\left(\frac{1}{T1} - \frac{1}{T2}\right)$, where

K_1 and K_2 equillibrium constrants

ΔH- the avarage heat of the forward reaction

T_1 - initial absolute temperature

T_2 - end absolute temperature

The characteristics of the polymer material for the rigid contact lenses and the official quality requirements for the article are proven to be related to the classical postulates of the physicochemistry.

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