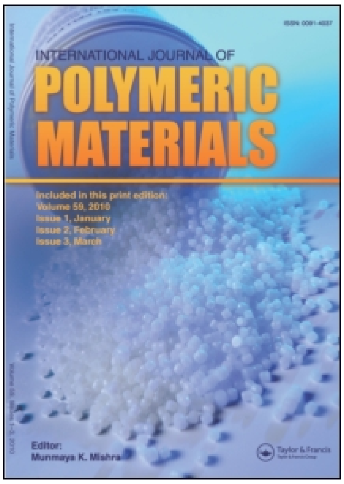

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Refractometric Investigation of Polymer Gradient Optical Media Based on Some Organic and Elementorganic Monomers

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Refractometric Investigation of Polymer Gradient Optical Media Based on Some Organic and Elementorganic Monomers

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(Received 10 April 1997)

A nondestructive refractometric method for determining the concentration distribution of a diffusing material into a light focusing polymer gradient elements (LFPGE) is developed.

Keywords: Gradient; gel-matrix; diffusant; focusing; refraction index; distribution; calculation; optical properties

INTRODUCTION

Light focusing polymer gradient elements (LFPGE) are the basic constituent of many information processing systems. The LFPGE is an optically transparent polymer rod with the parabolic distribution of the refraction indices as function of radius. It also has the light focusing and reflecting properties. LFPGEs are frequently used as the ending elements in the light guides communication lines and in the image transfering systems.

The LFPGEs are usually produced by the following procedure: the partly polymerized cylinder of the optically transparent network polymer with the higher refraction index (e.g., the gel-matrix) is placed

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*Corresponding author.

in the monomer diffusing with the smaller refraction index and then the obtained gradient of the diffusing medium concentration is fixed by thermocopolymerization [1 – 3].

The gel-matrices are frequently produced from the diallyl and diacrylate compounds and as diffusants we used the acrylates and fluoroacrylates [1 – 5]. Since there is a high demand for light, thermal, radiation and moisture resistant LFPGEs, are very suitable materials the organo-silicon and carboran containing polymers and copolymers are very suitable materials for this application.

For the fabrication of LFPGEs it is necessary to investigate the distribution of the diffusing medium versus the radius. This is especially critical for investigation of new systems of gel-matrices and diffusants. In these cases, the layer by layer fractional analysis over the element radius are usually performed [6, 2]. This permits us to determine the percentage of the network polymers, linear polymers and copolymers and also the residual monomers entering into the LFPGE composition. This method is precise, but very laborious and, what is significant, leads to the destruction of the sample.

RESULTS AND DISCUSSION

We developed the nondestruction method of the refractometric control for the point by point distribution of the diffusing material concentration into the transverse section of the LFPGE.

The method is based on employing of the dependence of refraction R from the refraction index n, which was substantiated by the quantum theory of dispersion [6]. In the article [7]. It was reported [7], that in a region of transparency the refraction index of one-component medium is expressed as

$$N = 1 + cN\sigma\tau, \qquad (1)$$

where c is the light velocity in the vacuum, N is the density of scatterers (the valence and conduction electrons), σ and τ are the cross-section and duration of the elastic photon-electron scattering at zero angle. The quantities, which characterize the elementary act of photon-electron scattering in the equation (1), can be expressed in terms of the macroscopic parameters of the medium: the refraction R, the density ρ, the molecular mass μ, the Avogadro number N_A [6].

For the multicomponent mixture it is convenient to use the coefficient of the molecular packing [8–10]:

$$K = (\rho/\mu)N_A \sum \Delta V_i, \tag{2}$$

where $\Sigma\Delta V_i$ is the sum of increments of the Van-der-Waals volume of the investigated media. The expression for the mixture of substances A and B is [6]:

$$n = 1 + \frac{3}{2} \cdot \frac{m_A(\sum R_i)_A + m_B(\sum R_i)_B}{m_A V_A + m_B V_B}, \tag{3}$$

where $V_{A,B} = (\Sigma\Delta V_i)_{A,B} \cdot 0,6023/K$ is the Van-der-Waals volume of molecules A or B: $(\Sigma R_i)_{A,B}$ and $m_{A,B}$ are their sums of refraction and mole fractions.

The equation (3) can be used to calculate the refraction index and, therefore, for evaluation of the concentration of either of components, provided the dependence of the refraction index n on coordinate r along the LFPGE transversal radius is known. (For the cylindrical LFPGE the refraction index distribution along this radius is determined by the standard method using the Mach-Zander interferometer [11].

The layer by layer fraction analysis of LFPGE's [1, 2] demonstrated that their main component is the network copolymer.

Evaluation of the space distribution of diffusing material was performed assuming that the LFPGE consists only of the network copolymer of matrix material (M) and diffusant (D). The network consisting of the monomer links M and D as calculable model system, can be represented by the random alternation of "dimers" $M-M$ and $M-D$, and expression (3) can be rewritten in the form

$$n = 1 + \frac{3}{2} \cdot \frac{(1 - m_{M-D})R_{M-M} + m_{M-D}R_{M-D}}{(1 - m_{M-D})V_{M-M} + m_{M-D}V_{M-D}}, \tag{4}$$

where R and V are the refractions and Van-der-Waals volumes of the "dimers", m_{M-M} and m_{M-D} are their mole fractions and $m_{M-M} = 1 - m_{M-D}$. From (4) it follows that

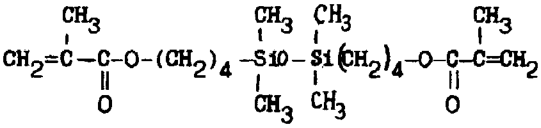
$$m_{M-D} = \frac{3R_{M-M} - 2(n-1)V_{M-M}}{3(R_{M-M} - R_{M-D}) - 2(n-1)(V_{M-M} - V_{M-D})}, \tag{5}$$

and the diffusant concentration in mole percents is equal to

$$m_D = 100m_{M-D}/2 - 50m_{M-D}; \quad \text{(mole \%)} \tag{6}$$

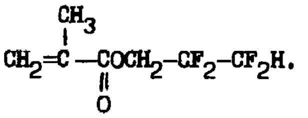
in any point of the LFPGE radius (r) if the value of the $n(r)$ in this point is known.

We calculated the distribution of diffusant concentration over the LFPGE radius, whose matrix was fabricated from the organo-silicon bifunctional monomer of the following structure



$$CH_2{=}C(CH_3){-}C({=}O){-}O{-}(CH_2)_4{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2(CH_2)_4{-}O{-}C({=}O){-}C(CH_3){=}CH_2$$

and as diffusant we used 2,2,3,3-tetrafluoropropylmethacrylate (4FMA):



$$CH_2{=}C(CH_3){-}C({=}O)OCH_2{-}CF_2{-}CF_2H.$$

For the calculation of the Van-der-Waals volume V, we used the values of ΔV_i, the published increments of the Van-der-Waals volume [8, 9, 11 – 13], or values calculated by the method reported elsewhere [9]. The values of these increments are presented in Table I. The calculation of the molecular refractions was performed using the reported values of refraction from [14, 15].

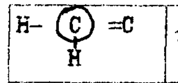
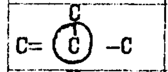
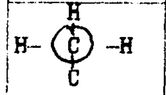
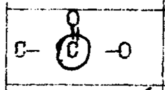
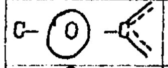
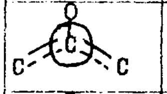
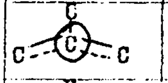
With these data we obtain the following values of Van-der-Waals volumes and refractions for the "dimer" $M-M$ and polymer 4FMA (DD):

$$R_{M-M} = R_M = 110,46; \quad R_{D-D} = R_D = 34,64,$$
$$V_{M-M} = V_M = 347,31; \quad V_{D-D} = V_D = 126.$$

In accordance with the formulae (3) it we obtain the following expression for the refraction index of the "dimer" $M-D$

$$n_{M-D} = 1 + \frac{3}{2} \cdot \frac{0,5R_M + 0,5R_D}{0,5V_M + 0,5V_D} = 1 + \frac{3}{2} \cdot \frac{72,550}{236,805},$$

TABLE I Increments of the Van-der-Waals volumes (ΔV_i) of singled atoms or atomic groups

	17,1
	9,0
	17,2
	15,9
	2,7
	11,65
	8,4
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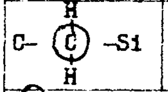
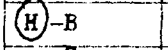
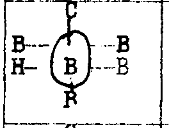
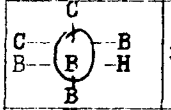
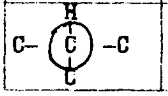
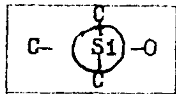
	11,9
	3,0
	3,8
	3,6
	9,0
	24,9
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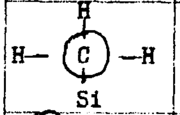
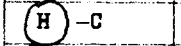
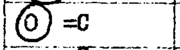
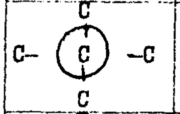
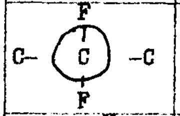
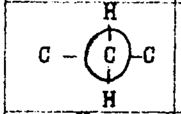
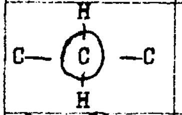
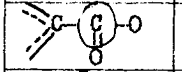
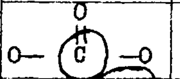
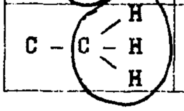
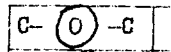
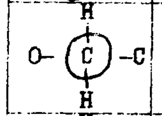
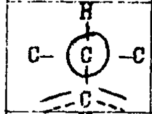
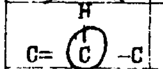
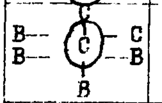
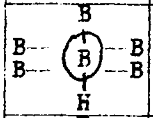
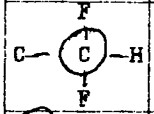
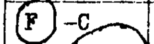
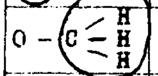
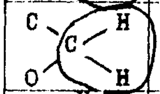
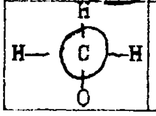
	16,0
	2,0
	5,85
	5,0
	9,1
	12,8
	13,1
	15,7
	19,0
	23,5
	3,4
	16,2
	8,7
	13,1
	3,35
	4,9
	5,1
	9,2
	26,3
	20,2
	20,3

which demonstrates that the refraction and Van-der-Waals volume of $M-D$ must be equal to

$$R_{M-D} = 72,55; \quad V_{M-D} = 236,805.$$

By substituting the calculated values of R_{M-M}, R_{M-D}, V_{M-M} and V_{M-D} into (5) with consideration of (6) we obtain the distribution of the diffusant m_D material versus the LFPGE radius. The corresponding curves of $m_D(r)$ and $n(r)$ are presented in Figure 1.

The proposed method of the $m_D(r)$ calculation was also applied to the LFPGE from the material pair diallyl isaphthalate-fluoroacrylates (DAIP)-4FMA and diethyleneglycol-bis-allylcarbonate-fluoroacrylates (DEGBAC)-4FMA [16, 17], the corresponding curves of the diffusant refraction index and mole fraction versus LFPGE radius are given on the Figures 2 and 3.

For the LFPGE obtained under the mutual diffusion of bifunctional monomers, the polymer rod has a fully network structure containing no linear segments of homopolymers and copolymers.

For the investigated DAIP-diallyl sebacinate (DAS) and DAIP-DEGBAC systems we calculated the distributions of the diffusant concentration for the cases of; a common probable copolymer structure of matrix and diffusant materials, and the system represent-

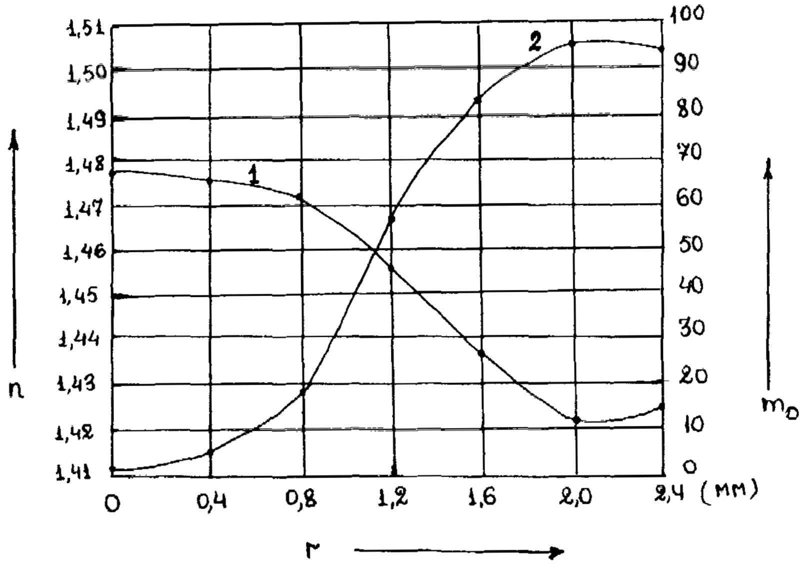


FIGURE 1 The dependence of the refraction index value (curve 1) and mole fraction of the diffusant 4FMA (curve 2) versus radius of the LFPGE on the basis of matrix from bifunctional organosilicon monomer.

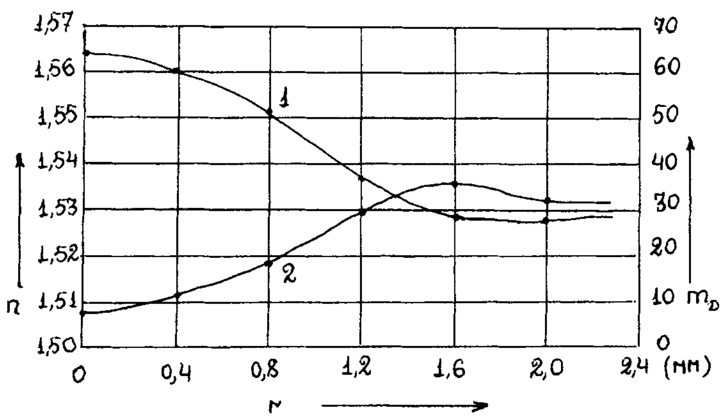


FIGURE 2 The dependence of the refraction index value (curve 1) and mole fraction of the diffusant 4FMA (curve 2) versus radius of the LFPGE on the basis of matrix from DAIP.

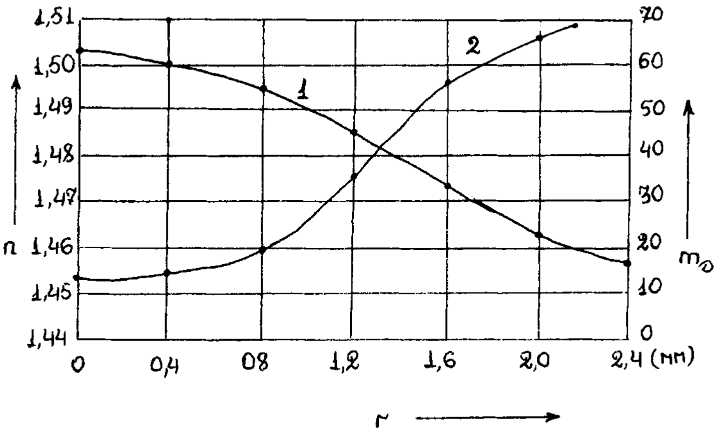


FIGURE 3 The dependence of the refraction index value (curve 1) and mole fraction of the diffusant 4FMA (curve 2) versus radius of the LFPGE on the basis of matrix from DEGBAK.

ing an apparent interpenetrating network-IPN. In the latter case the model system of calculation assumes the "mixture" of matrix and diffusant polymers. The dependences of the refraction index profile and diffusant mole fraction versus the LFPGE radius are presented in the Figure 4. As it is seen from this Figure the calculations for the network copolymer and IPN model give very similar results.

Organosilicon bifunctional monomer used for the LFPGE gel-matrix fabrication forms polymer with the refraction index $n = 1{,}4771$. Therefore, if similar materials are used for gel-matrices it is necessary to select diffusants with lower refraction indices. This can be achieved with fluoroacrylates. It is also desirable to select materials for gel-matrices, which combine the proper optical, technological and operation properties of the organosilicon polymers but have a higher refraction index. A convenient way to obtain such materials is their

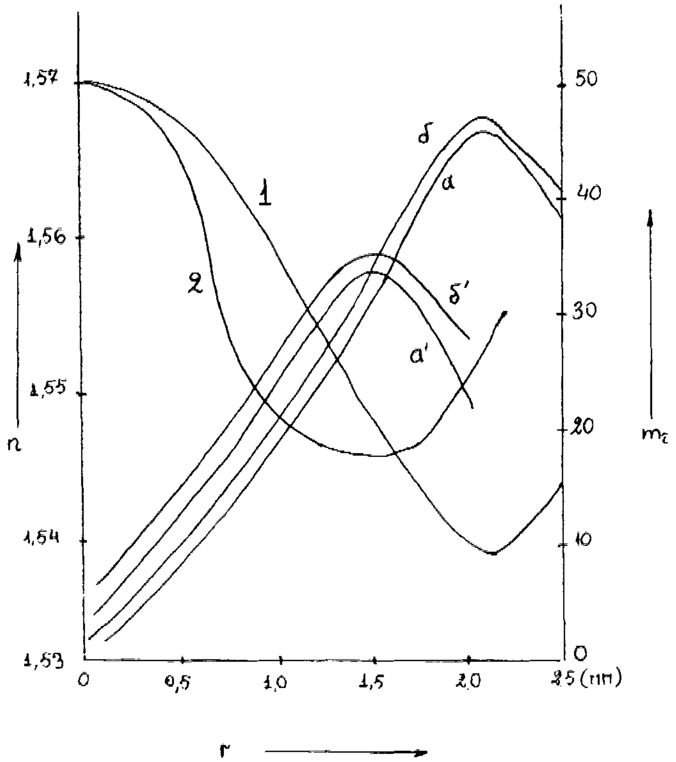


FIGURE 4 The dependence of the refraction index value and mole fraction of the diffusant DEGBAK (curve 1) and DAS (curve 2) in the DAIP matrix versus the LFPGE radius: the curves a and a', are for the estimated model of the network copolymer, b and b' are for the estimated model of IPN.

copolymerization with styrene. Due the expression (3) and data from the Table I and [14, 15] for the copolymers composition:

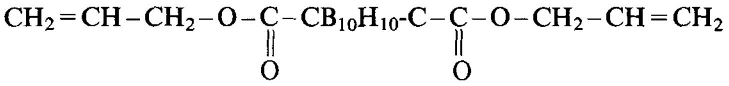
50 : 50
styrene : organosilicon diacryllate 70 : 30 (mol.%)
30 : 70

we obtain the refraction indices

$$n(50:50) = 1,500;\ n(70:30) = 1,518;\ n(30:70) = 1,488$$

The first two of are higher, then the polymethylmetacrylate with ($n = 1{,}49$), which is now the most frequently employed diffusant.

It is conceivable that the highest refraction index may has the transparent of bifunctional monomer of such structure [18]:



$$CH_2=CH-CH_2-O-\underset{\underset{O}{\|}}{C}-CB_{10}H_{10}\text{-}C-\underset{\underset{O}{\|}}{C}-O-CH_2-CH=CH_2$$

Calculation of the refraction index for this monomer is performed analogically with usage of the data from the Tables 1 and [14, 15] and leads to $n = 1{,}580$, which value permits to prefer to this diffusant monomer from some classes of investigated materials [17].

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