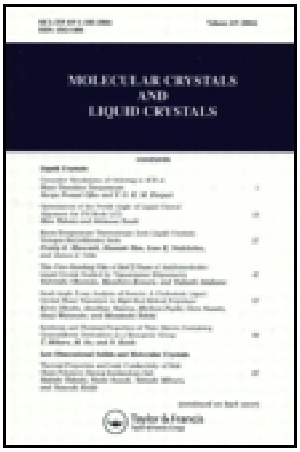

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Optical Properties of Liquid Crystals in Porous Glasses

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OPTICAL PROPERTIES OF LIQUID CRYSTALS IN POROUS GLASSES

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Abstract This paper presents the results of investigations of light scattering and transmission in porous glass–liquid crystal (LC) and polymer systems. It was shown that for cholesteric LC in macropores (unlike the nonmesogenic system isotropic liquid-porous matrix) polarized component of scattered light intensity cannot be described by the sum of intensities caused by: doublescattering, scattering by the matrix, scattering due to the refractive index mismatch between LC and the glass, scattering by the density and the order parameter fluctuations. The existence of essential surplus light scattering, its dependence on the wave number and results of temperature measurements are explained with the only assumption that LC in pores at temperatures above the critical one is pseudotwo phase system with anisotropic interphase layer on pore walls arrising as result of orientational wetting. The interpretation of the results of optical investigations of comblike polyalkylmethacrylates in macroporous glasses is based on the suggestion of the existence of orientational order in the arrangement of relatively long side radicals, which is induced by the pore surface.

INTRODUCTION

The progress attained in the investigation of surface properties of liquid crystals and the topicality of these investigations have been convincingly shown in ref.[1] The information about the surface properties and size effects in liquid crystals may be obtained most effectively by investigating these substanses in porous matrices. Films containing microdroplets of LC distributed in polymer and glass matrices have recently been described.[2-10] The difference between the surface and bulk properties of a material may be of fundamental importance and can be manifested near the surfaces of new phases which are not present in the bulk and by transition between these phases. The presence of finely porous matrices with developed interior pore surface, the area of which is about 10^6 cm^2 per cm^3, and which are transparent at visible wavelengths, and also the presence of LC, the refractive index of which in the isotropic phase is close to the corresponding value for the matrix, enable us to pursue the investigations by optical methods, which are exceedingly sensitive to phase transitions and to any structural changes in the substance.

The synthesis and investigations of polymers in porous matrices are of considerable interest because in these systems the difference between surface and volume properties of polymers may differ greatly because in these systems the filler particles may be in the colloid degree of dispersity, and the role of the interface becomes very great and the expected effects caused by the orienting action of the solid surface on the macromolecule or its fragments may be most pronounced. The present paper deals with the investigations of the temperature and wave number dependences of light scattering intensity for LC in pores and temperature and spectral dependences of light transmission coefficient for polymers in pores. The interpretation of these results for polymers is based on the suggestion about the existence of orientational order in the arrangement of relatively long side substituents,which is induced by the pore surface.

SAMPLES AND EXPERIMENTAL PROCEDURE

Porous matrices with through - pores were prepared from the original sodium borosilicate glasses: the sodium borate phase was removed by leaching and the matrix framework consisted of SiO . Two types of matrices were used. Their characteristics, pore average size <l>, volume fraction ω and specific surface area S/V, were determined by small-angle X-ray scattering and had the following values: <l> = 120 Å, ω= 0.27 , (S/V) = 100 m per 1 cm and <l> = 1000 Å,

ω= 0.38 and (S/V) = 28 m^2 per 1 cm^3 for micro- and macroporous matrices, respectively. The temperature dependences of the polarized I_V^V and depolarized I_H^V components of scattered light intensity were measured at scattering angles between 30° and 160°. As light sources we used a He-Ne laser (= 6328 A) and an argon laser (λ= 5145 Å, λ= 4658 Å). The scattering characteristics were measured on porous glass cylindrical samples 5 mm in diameter and 4 cm high, which were mounted in the cylidrical cell in such a way that the cell and the sample were coaxial. The pores and the free space between the sample and the cell wall were filled with liquid under investigation. These measures prevented the liquid from leaking out from the pores.We investigated cholesteric LC with the temperature of the transition to the isotropic phase T = 35 °C.The choice of given LC is determined by the fact that refractive index of cholesteric LC is closer to refractive index of matrix material then in LC of other type. Temperature dependence of the scattered light intensity in isotropic phase of this LC have been investigated thoroughly.[11] Benzene and toluene were used as typical isotropic liquids for comparision with LC. The relative error in the determination of intensity did not exceed 2% and the temperature of the cell was stabilized and measured to within ± 0,05 °C. In order to establish the relationship between the length of the side substituent in the homologous series of polyalkyl methacrylates and polymer structure in pores, silicate porous glass matrices were used to synthesize n-alkyl methacrylates (MA-i): methyl methacrylate (i = 1), ethyl methacrylate (i = 2), butyl methacrylate (i = 4), octyl methacrylate (i = 8), decyl methacrylate (i = 10), 2 - ethyl hexyl acrylate, and styrene.

The spectral dependence of light transmission coefficient A was measured for all samples in the wavelength range from 380 to 1000 nm at various temperatures.

An SF - 26 spectrophotometer was used for the measurement of light transmission coefficient. Its cell part was modified in such a manner that temperature could be varied from 20 to 120 °C. It was also possible to thermostate the sample and to measure its temperature to within ± 0.1C. The samples were polished porous plates with the polymers in pores. Their thickness was 1 mm.

It should be noted that porous quartz glass can be used as an ideal matrix to study the influence of temperature on the surface effects that occur at the interface between the glass and the second component. Since the structural characteristics of the quartz matrix are nearly independent of the temperature, all the observable effects can be attributed to the change in the physical properties of the second component.

LIGHT SCATTERING IN MACROPOROUS MATRIX

An electron micrograph of macroporous matrix revealed some order in the arrangement of the elements of the solid phase. The high packing density of the regions of inhomogeneity in porous glasses and their phase separation mechanism itself can cause ordering in the arrangement of the inhomogeneities and lead to the generation of a modulated structure. For the optical measurements, the pores were filled with an immersion fluid. As the immersion fluid we used benzene at 53,7 °C. At this temperature the dependence of I_V^V on $[n_m - n(T)]$, where n_m is the refractive index of the porous matrix material (which is assumed independent of temperature) and $n(T)$ is the temperature-dependent refractive index of liquid, has minima (Fiq. 1), and temperature dependend intensity (I_V^V) is proportional to $[n_m - n(T)]^2$. At $T = 53,7\,^\circ C$ the sample became transparent and had blue color. Line 1 in Fiq. 2 shows the correlation function $\varphi(q)$ as a function of the wave number according to the measurements of the polarized component of the intensity of the scattering light. For this purpose, we wrote the measured intensity $I_V^V(\theta,\lambda)$ in the form

$$I_V^V(\theta,\lambda)=\mathrm{const}\,\varphi(q)/\lambda^4,$$

where $\vec{q}=\vec{k}_i-\vec{k}_s$, $q=(4\pi n/\lambda)\sin\frac{\theta}{2}$ and $\vec{k}_i$ and $\vec{k}_s$ are the wave vectors of the incident and scattered light.

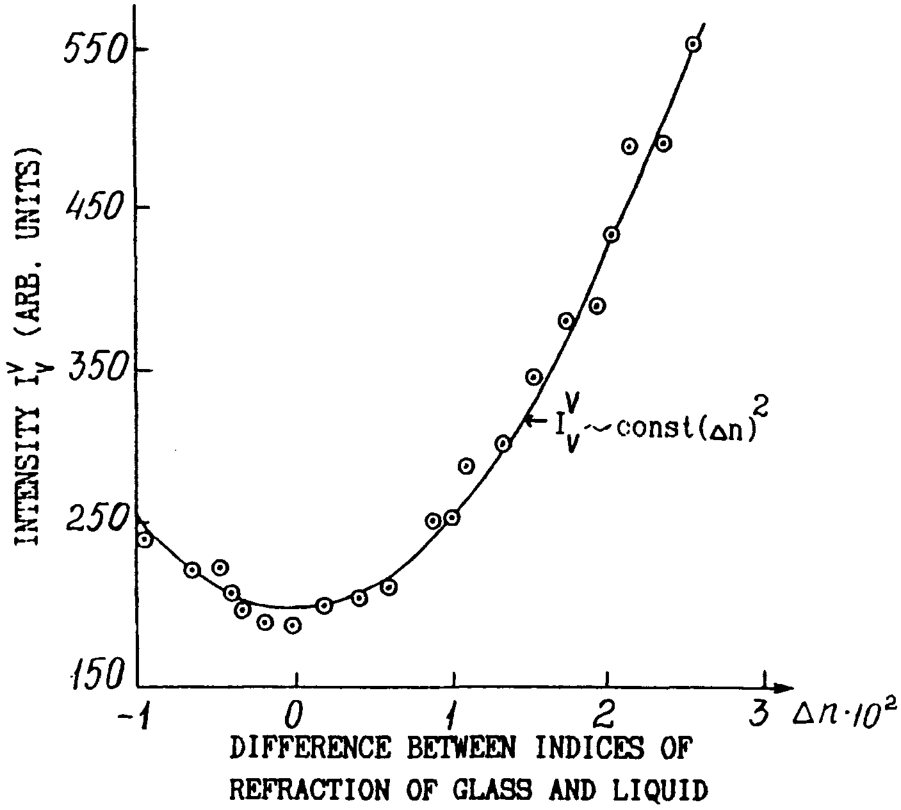

FIGURE 1 Intentity of scattered light vs refractiv index mismatch

It follows from the behaviour of the function $\varphi(q)$ that for scattering angles $\approx 90°$ the intensity of the optical scattering (the factor of $1/\lambda^4$ is taken into account) for the blue light is nearly an order of magnitude greater than that for red light. This is the reason for the characteristic of the blue color. We showed[10] that any transparent structure having a correlation function of this sort should exhibit blue color. Line 2 in Fig.2 show the result of light scattering measurements for the blue phase of cholesteric LC.

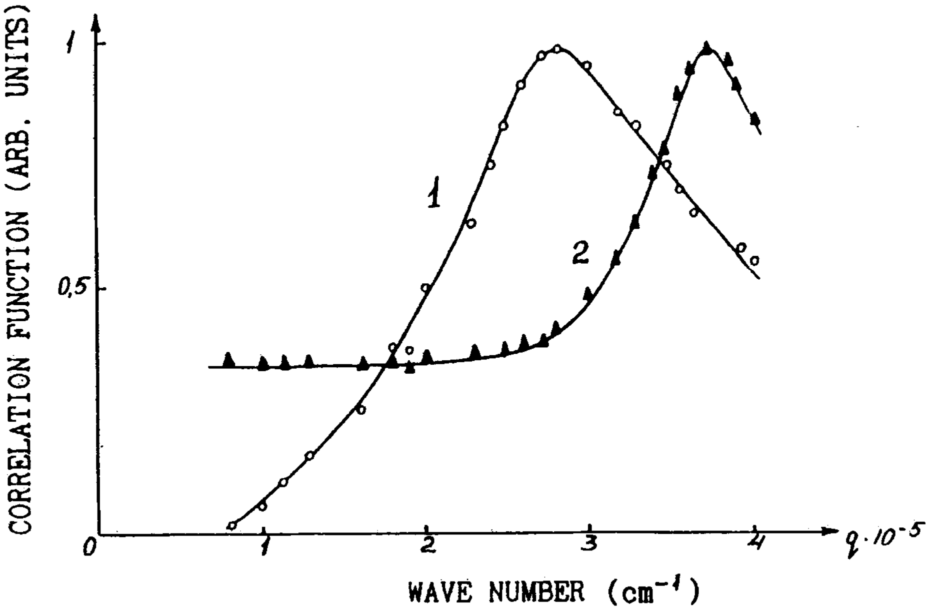

FIGURE 2 Correlation function as a function of the wave number. 1-macroporous glass impregnated with benzene; 2-Blue phase

This line, like the line for macroporous glass has maxima, and correlation functions of macroporous glass filled with an immersion fluid and blue phase are analogous. The positions of these maxima correspond to a characteristic dimensions 2200 Å and 1700 Å respectively.

LC IN MACROPOROUS MATRIX

It is natural to assume that intensity of the scattering light I in system LC - porous matrix is determined by the sum of intensities:

$$I = I_m + I_{\Delta n} + I_\rho + I_\eta + I^{(2)}, \qquad (1)$$

where I_m, $I_{\Delta n}$ are scattering by matrix and scattering due to the refractive index mismatch between the LC and the glass; I_ρ, I_η are contributions due to density and order parameter fluctuations and $I^{(2)}$ is intensity of double scattering. The evaluation of values of contributions in total intensity were carried out at scattering angle $\theta = 90^\circ$. Contribution $I_\rho + I_\eta$ can be evaluated by measuring light scattering intensity I in system under investigation and I_{is} - intensity in isotropic phase of LC in free state, because I_{is} is determined[11] by sum $I_\rho + I_\eta$. In temperature range 45-55°C the experiment resulted in: $I/I_{is} \sim 10^3$.

Consequently at temperatupes far from the temperature of phase transition items I_ρ and I_η in formula (1) can be neglected i.e. molecular light scattering is negligible small. The measurements of double scattering results in: $I^{(2)} \approx 0{,}25\ I$. It is unable to exclude $I_{\Delta n}$ by selection of temperature because the refractive index of LC will coincide with refractive index of matrix framework at temperatures higher then 100°C. For the estimation of the effects of I_m and $I_{\Delta n}$ on the intensity I measurments to compare light scattering in the sample under the investigation at the temperature of 52,8°C and in the same matrix impregnated with toluene at T = 20°C were carried out.

Under these temperatures the rerfective indices of toluen and LC coincide with an accuracy up to the third digit, i.e. if we neglect the dependence of n on temperature, the differences between the refractive indices of substances, filling the pores and the matrix are equal and correspondingly I are equal as well. The scattering of the matrix does not depend on the pore filling substance, and accordingily $I_m + I_{\Delta n}$ in both systems are equal under equal Δn. The light scattering intensity in tocuene-porous matrix system is also determined by the formula (I). We may conclude from the experiment, that $I^{(2)}$ in this system constitutes, 1/3 of $I^{(2)}$ in LC-porous matrix system. Taking into account this fact and neglecting the molecular scattering in toluene it is possible to determine the sum $I_m + I_{\Delta n}$ from the measurement of total intensity in the toluence-matrix system and this sum, in this given case, is equal to the above-mentioned sum in the LC-matrix system. This value makes up about 30% of the total intensity I in the LC-matrix system. Thus from the total body of the conducted experiments for the LC-matrix system we have the following results: $I^{(2)} = 0{,}25\ I$, $I_m + I_{\Delta n} = 0{,}3\ I$ and the sum $I_\rho + I_\eta$ is insignificantly smaller compared to Bthe full intensity I, i.e. there is a substantial surplus scattering $\delta I = 0{,}45\ I$, which hasn't been included in the formula (1). Thus, at the scattering angle of $\theta = 90°$ the light scattering in the LC-matrix system could not be described within the framework of the supposition about the nature of scattering determined by formula (I). It was shown above, that in the system macroporous glass - isotropic nonmesogenic liquid the intensity of scattered light strongly depends on the wave number q and has wide maximum at $q = 2{,}8{*}10^5\ cm^{-1}$ therefore, in order to determine whether the existance of the excessive intensity I in LC-matrix system has not resucted from differences between I(q) in both systems: LC--matrics and toluene matrix it is necessary to study the angular dependency of the intensity of scattered light in these systems under equal Δn. These dependence I(q), provided, that we have taken into account-double scattering under $\Delta n = 0{,}024$ are represented in Fig.3 (curves 1 and 2). It is clearly seen, that these curves have an analogous form. This form coincides with the form of the curve, which is described by a correlation function, determined by the matrix structure. As followus from Figure 3, the surplus scattering is observed under all q (curve 3) and the form of I(q) is analogous to the form of curves 1 and 2. Two main peculiarities of light scattering in LC-matrix system: the existence of surplus scattering δI and the dependence of $\delta I(q)$ could be explained by the following supposition.The surface layer, the scattering properties of which are different from the respective properties of LC - in the remaining non-surface volume, is formed on the porous walls. And this is the reason of the appearance of δI. The form of the layer in every pore and their respective arrangement are determined by the shape of the pores and the matrix structure this determines the dependence $\delta I(q)$.

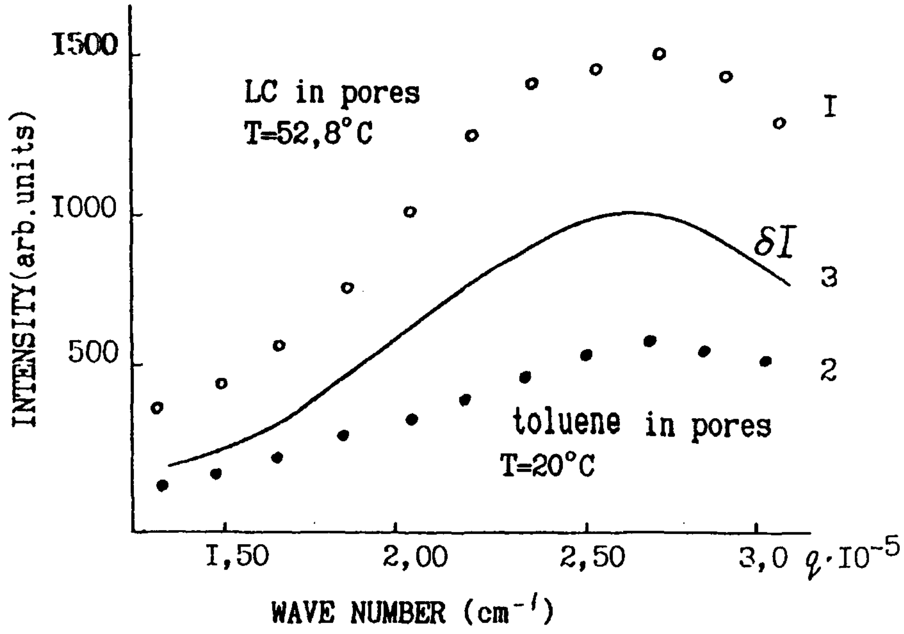

FIGURE 3 Intensity vs wave number: 1-LC in macropores; 2-toluene in macropores; 3-surpluse scattering

The supposition about the existence of the interphase layer, appearing on the interphase glass (wall of pore) - - LC - is confirmed by the resultis of measurement of temperature dependense of scattred light intensity. The dependence of I on n are represented in Fig.4 for the systems under consideration. The range of changes of Δn = 0,025-0,029 for the LC-matrix system corresponds to the changes of T(55-45 °C) and for toluene-matrix systems (22-13 C). For toluene the dependence I(T) could be approximated by the expression $I = I_m + I_{\Delta n}$ in accordance with formula (1), where $I_{\Delta n}$= const$(\Delta n)^2$, as it should be for the isotropic liquid (Fiq.1).

As it is seen from Fig.4, the temperature dependece of I is not observed within the experiment accuracy. This effect is in full accord with the previous supposition about the existence of LC surface layer in pores and optical and structural properties of this layer are independent of the temperature in the studied temperature range.

The appearance of the interphase layer and the difference of its properties from the bulk properties are due to the orientational influence of the solid surface of the pore.

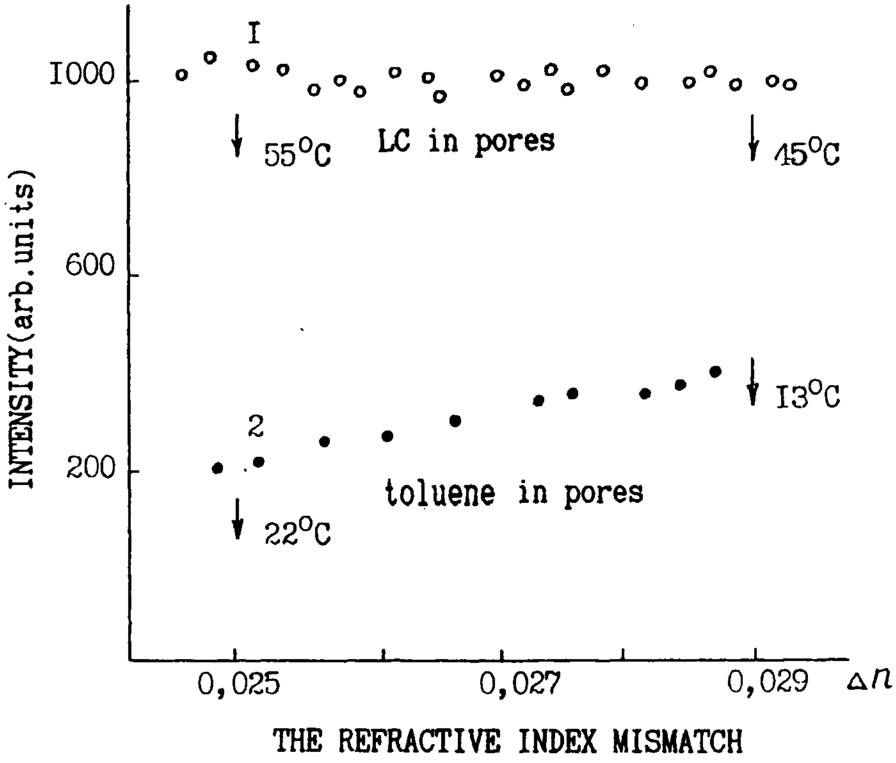

FIGURE 4 Intensity vs refractiv index mismatch: 1-toluene and 2-LC in macropores

This influence at distances of 10^2 Å causes anistropy and the surface alignment of LC even uder temperatures, corresponding the isotropic phase of a free LC.

Thus, the difference of scattering properties of the LC surface layer is connected not only with the refractive index chance due to the molecule orientation by the surface and additional mechanism as well: by the fluctuation of the local director, which determines the wall-induced preferential alignment of molecules.

This, the lack of the dependence $I(T)$, the existence and the character of the dependence $\delta I(q)$, prove the existence of the surface layer with an orientational order even at temperatures, corresponding to the isotropic phase of free LC, the orientationally ordered surface layer determines the optical properties of LC in pores significantly. The temperature dependence of I_H^V is represented in Fig.5. We found that there was a pronounced change in the intensity at temperatures 37-39 °C. If the temperature 38 °C corresponding to peak is interpreted as the phase transition temperature T_{c2} from LC to isotropic phase, we may make the conclusion that the pores tend to create an orientational order and increase T_c in pores compared with the corresponding value for LC in free state.

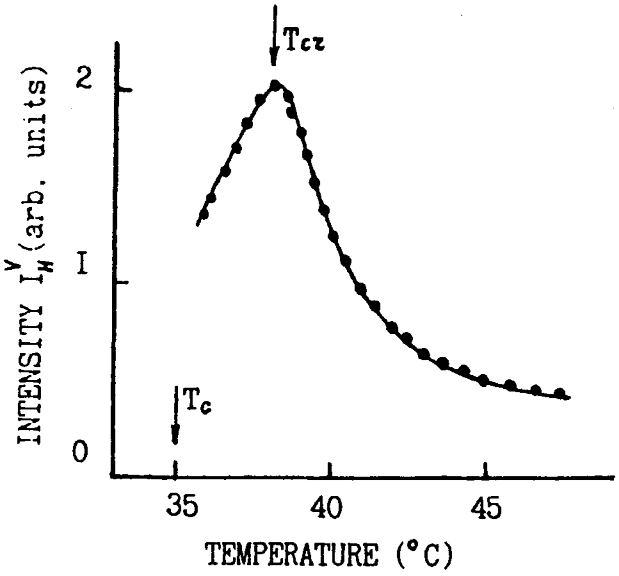

FIGURE 5 Intensity vs temperature in LC-macroporous glass system.

The increase of T_{cr} can be explained qualitatively by the orienting influence of the pore surface on molecules, which stabilizes the orientational order. In a quantitative description of this effect we must take into account the contribution made to the bulk density of the free energy by the anisotropic part of the surface energy, which is due to the poBlar order and is given by

$$F_{0r} = -W(\vec{n}\vec{\nu})S/V \;, \qquad (2)$$

where $\vec{\nu}$ is the normal to the surface, $\vec{n}$ is the director, and W is the anisotropic part of the surface energy of the liquid-crystal phase (representing the energy of adhesion of a liquid crystal to its substrate), which vanishes for the isotropic phase.

The condition of equilibrium of the phases subject to Eq.(2) is of the form

$$F_{NV} + \sigma_N S/V - W(\vec{n}\vec{\nu})S/V = F_{IV} + \sigma_I S/V \;, \qquad (3)$$

where F_{NV} and F_{IV} are the bulk terms of the free energy in the nematic and isotropic phases, and σ_N and σ_I are the corresponding surface tension coefficients. Bearing in mind that $F_{IV} - F_{NV} = q\rho(1 - T_{cr}/T_c)$ and $S/V = 2/R$ for a cylindrical pore and that $\sigma_{NI} = \sigma_N - \sigma_I$ and also assuming that under the equilibrium conditions we have $\vec{n}\vec{\nu} = 1$ ensuring the minimum of F_{0r}, we fild that the shift of the temperature of the transition to the isotropic phase is

$$T_{cr} - T_c = 2T_c(W - \sigma_{NI})/q\rho R \;, \qquad (4)$$

where q is the heat of the transition from the nematic to the isotropic phase, which has the value $2 \cdot 10^7$ erg/g typical of nematic liquid crystals. The values of W calculated using Eq.(4) are close to 1 erg/cm^2

POLYMERS IN MACROPOROUS MATRIX

When light transmission through porous-glass plates the pores of which contain poly(alkyl methacrylates) with a long side substituent was studied, anomalous change in light scattering in a narrow temperature range ΔT was observed. Fig.6 shows the temperature dependence of the transmission coefficient A measured at a wavelength $\lambda = 550$ nm for macroporous glass-polymer systems.

It is clear that for PEHA A increases by two orders of magnitude when T increases from 45 to 60 °C and decreases to the initial value with decreasing T. Since light absorption by the matrix and the polymers is absent at $\lambda = 550$ nm, the observed dependence A(T) is caused by the change in the intensity of scattered light with temperature. This behaviour of A is characteristic only of polymers with a sufficiently

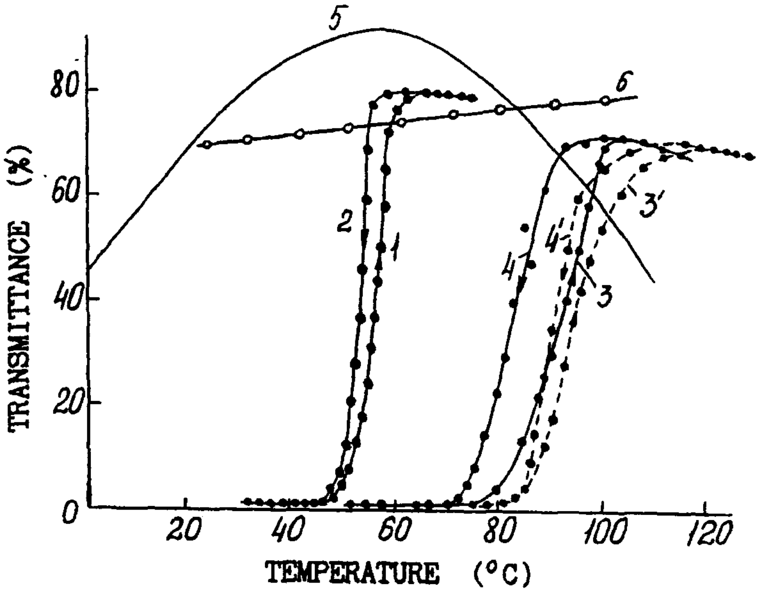

FIGURE 6 Light transmission coefficient vs T for the following systems: macroporus glass – 1, 2) PEHA, 3', 4') PMA-8, 3, 4,) PMA-10, 6) PMA-1, 5) calculated curve for PMA-10

long side radical (i = 8 or 10) and cannot be explained by the differences in the temperature dependences of refractive indices of silicate matrix ($dn/dT \approx 10^{-6} deg^{-1}$) and polymers filling the pores ($dn/dT \approx 10^{-4} deg^{-1}$) as in two-components systems consisting of isotropic substances. This can be seen in Fig.6 where curve 5 is calculated for PMA-10 in macroporous glass with the assumption that the extinction coefficient is $\sigma = const(\Delta n)^2$

One of reasons for anomalous light scattering may be the orientational ordering of side substituents induced by for PMA-i in the free state at i > 12 . In contrast to systems with the side substituent of the polymer (i = 8 or 10), in systems containing PMA-1,2,4 and PS, the change in A with temperature is related to the temperature dependence of the refractive index of the polymer. The dependence A(T) typical of the latter systems is shown in Fig.6 by curve 6 for poly (methyl methacrylate).

The concept of the formation of orientationally ordered regions in PEHA, PDMA, and PDMA near the inner pore surface is in good agreement with the molecular structure of these polymers and with that of the surface layer of silica. Its surface contains a large number of SiOH groups. The molecules of poly(alkyl methacrylates) contain ester group including the C=O bond. The oxygen atom of the carbonyl group of the macromolecule forms a hydrogen bond with the hydrogen atom of the silanol group, and the polymer chain should be arranged on the silica surface, i.e. on the pore surface. As a result, relatively long side substituents placed on one side of the limiting surface should be mutually oriented. The orientation of side substituents of poly (octadecyl methacrylate) normal to the quartz (silica) surface has been detected by IR spectroscopy in monolayers of this polymer prepared by the Langmuir - Blodgett method.

In the condensed state the order induced by the wall to the nonmesogenic system can be retained at distances exceeding the characteristic geometrical size of oriented particles. The character of the A(T) dependence and the temperature hysteresis suggest that in the range of temperatures in which the transmission coefficient changes abruptly, spread first-order phase transition is observed. This suggestion was confirmed by calorimetric data.

Calorimetric measurements (DSC) for PEHA in macropores show that the thermogram exhibits two peaks: an endothermic peak upon heating and an exothermic peak upon cooling. The specific heat corresponding to these peaks is 3 J/g.

Similar endothermic and exothermic peak spreading with respect to temperature is observed for POMA in a macroporous matrix. The value of the corresponding thermal effect is 3.4 J/g. As for PEHA, the temperatures at which the peaks appear coinside with those at which the sample becomes transparent (upon heating) or cloudy (upon cooling).

The presence of temperature hysteresis on curve A(T) and calorimetric measurements indicate that for comblike polymers synthesised in pores a spread first-order phase transition is observed with a thermal effect characteristic of the trasition from the liquid-crystalline into isotropic Bstate.

Hence, in macroporous matrices in the pores of which a polymer with relatively long side substituent is synthesised, the orientational order is generated in their arrangement induced by the pore surface.

OPTICAL PROPERTIES OF POLYMERS IN MICROPORES

In microporous matrices the above effects are not observed. The spectral dependence of extinction coefficient for PMA-i ($i<8$) and for PS satisfies the relationship in accordance with Rauleigh's theory of light scattering. This result is natural because the characteristic size of optical inhomogeneity in microporous matrices may be taken to be equal to the pore radius, which is much smaller than the wavelength of optical radiation, and light scattering is the Rayleigh scattering. In the investigation of substances obtained in the synthesis of PEHA in microporous glass, macroscopic structures were detected with the size exceeding the wavelength of the visible light. Fig.7 shows the photograph of this typical macrostructure. Light scattering in these systems occurs on macroscopic inhomogeneities. It should be noted that in many cases the microporous glass-liquid crystal systems exhibit anomalous light scattering which cannot be explained by optical inhomogeneities caused by the difference in refractive indices of the matrix framework and liquid crystal or by molecular light scattering. One of the reasons for anomalous turbidity in these systems is the formation of clusters, which should be accompanied by intensive light scattering.

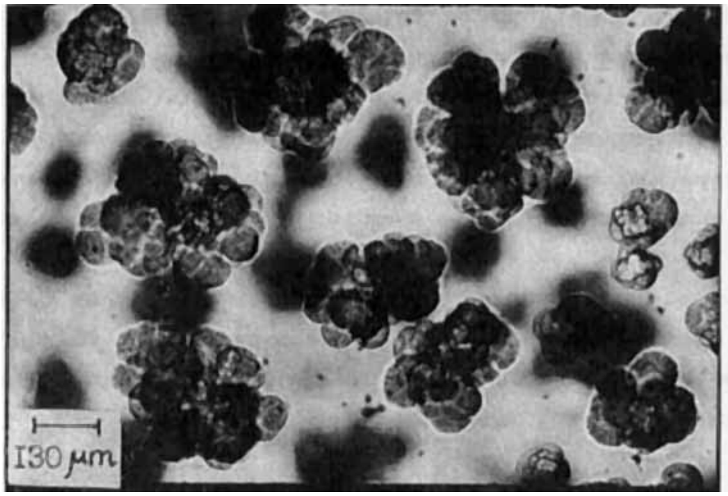

FIGURE 7 Photograph of clusters in the microporous glass - PEHA system

The spatial distribution pattern shown in Fig.7 is three - - dimensional. The dark spots on the photograph correspond to macroclusters located lower or higher than the focusing plane. High optical density of clusters prevents a precise calculation of the dependence of the cluster size on the number of particles contained in it and hence the determination of its fractal dimensionality. However, the picture shown in Fig.7 does not contradict those appearing in computer simulation of optically dense fractal clusters with fractal dimensionality about 2.5 inserted into the three-dimensional space.

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