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Polarization-interference micromethod for the study of mutual diffusion in polymer systems

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SUMMARY

A polarization-interference technique is developed for the study of mutual diffusion that is applicable to systems covering the whole concentration range from polymer - low-molecular-weight compound systems to polymer - oligomer systems. The technique is based on variations of the refraction index within the diffusion zone and is shown to have advantages over similar ones. Its accuracy in terms of wavelength is 0.04 . The polybutadiene - dioctyl phtalate system is used to illustrate how the concentration distribution of the components is calculated.

INTRODUCTION

Optical methods have now been established as a practical means for studying diffusion processes in polymer systems. They are based on measurements of either the refraction index n or its gradient dn/dx within the diffusion zone. There are both interference (e.g. the multibeam interference and interference-polarization method by Tsvetkov (1,2)) and refractometry methods (3,4).

The technique to be described was developed to study mutual diffusion processes in polymer systems. It makes use of a polarization-interference optical system, which can be used to measure the refraction index variation within the diffusion zone. Unlike other devices of the same kind the initially polarized light beam is separated into its ordinary and extraordinary components, which have a path difference between them, as soon as it has left the sample. The system yields the high locality and small dimensions characteristic of multibeam interferometers (1) and the sensitivity to variations in n that is characteristic of Tsvetkov's device (2). The technique at issue was not reported as practicable for diffusion measurements before.

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DESCRIPTION OF THE TECHNIQUE

The optical route of our microscope is shown in Fig.1. The main component is the polarization-interference unit, which consists of a Vollaston doubling prism, a polarizer, an analyzer, and a slit diaphragm. The prism is to separate the initially polarized light beam that has passed through the sample into two polarized ones: ordinary and extraordinary beams, and to introduce a phase shift between them. The angular separation of these beams r increases with increasing refracting angle of the prism. The slit is adjusted so that it is parallel to the refracting face of the prism. Together with the condenser the slit forms a collimator; parallel beams of coherent light leave it to interfere in the visual field of the microscope.

The interference pattern is formed as follows. Let the sample under study have a diffusion zone within which the refraction index n changes from n_1, the index of the pure low molecular weight component to n_2, the index of the pure polymer. When the light beam polarized by the polarizer passes throughthe sample, it acquires a definite phase lag which varies within the diffusion zone. This wave reaches the objective and is separated into ordinary and extraordinary waves which are caused to diverge at some small angle, these waves

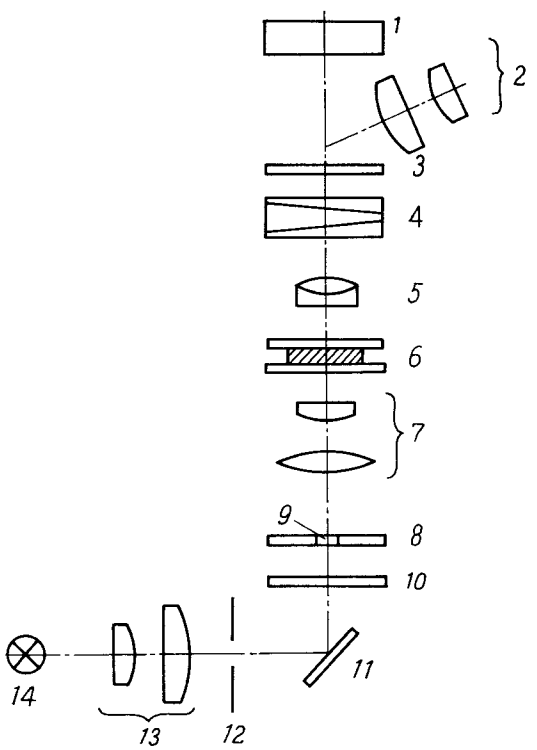

Fig.1 Optical route of a polarization-interference microscope:
1) camera
2) eyepiece
3) analyzer
4) Vollaston prism
5) objective
6) sample
7) condenser
8) slit diaphragm
9) slit
10) polarizer
11) mirror
12) field diaphragm
13) collector
14) light source

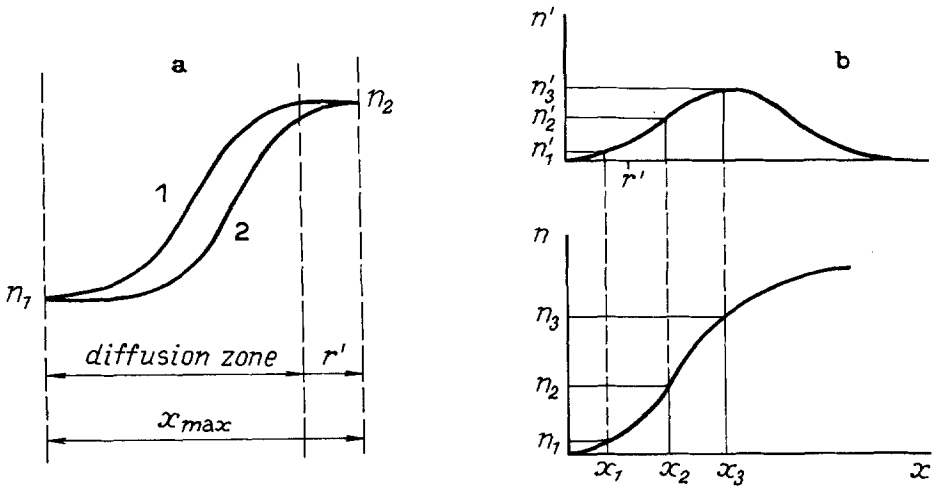

Fig.2 (a) Superposition of (1) an ordinary and (2) extraordinary waves and (b) the calculation of the refraction index variation within a diffusion zone.

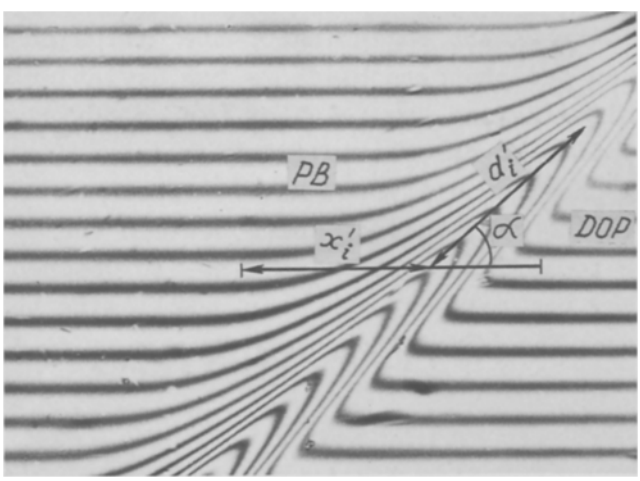

Fig.3 Photograph of the interference pattern in the polybutadiene (PB) - dioctyl phtalate (DOP) system at 20°C. The diffusion time is 16 min.

being polarized in perpendicular planes. No component of the waves other than that parallel to the direction of light vibration of the analyzer itself can be transmitted through it.

This means that after the waves have passed through the analyzer two waves are produced that are linearly polarized in parallel planes, Fig.2,a. These waves can interfere to form a pattern in the image plane of the microscope. The pattern will consist of straight interference bands if n=const outside the diffusion zone, and the pattern will be distorted inside the diffusion zone where n=const (Fig.3). To give rise to deviations in the interference bands in the diffusion zone it is necessary to adjust the initial boundary between the components at an angle α to the bands.

The refraction index variation within the diffusion zone is calculated by the following procedure. At first the distances between the beginning of the diffusion zone and several points within it are determined from

$$x_i = x_i^{*} \sin\alpha, \quad i = 1,2,3,... \tag{1}$$

and the corresponding difference between the refraction indexes of the ordinary and extraordinary waves

$$\Delta n_i^{*} = \frac{d_i^{*}\lambda}{hl} \sin\alpha , \quad i = 1,2,3,... \tag{2}$$

where λ is the wavelength of the light source; l is the thickness of the sample; h is the distance between the bands; x_i^{*} is the distance between the beginning of the diffusion zone and the i-th point on the photograph; d_i^{*} is the deviation of the band at this point. Having the relation $\Delta n_i^{*} = f(x_i)$ the refraction index profile is calculated (Fig.2,b): for any point x_1 satisfying the inequality $0 \leqslant x_1 \leqslant r^{*}$ (where $r^{*} = r\cos\alpha$ and r is the magnitude of shift between the two images) $\Delta n_1 = \Delta n_1^{*}$ is defined. The value Δn_2 is defined $\Delta n_2 = \Delta n_1^{*} + \Delta n_2^{*}$ for the point $x_2 = x_1 + r^{*}$. Following this procedure the value of Δn_i for any point $x_i = x_1 + (i-1)r^{*}$ is calculated from

$$\Delta n_i = \sum_{k=1}^{i} \Delta n_k^{*} , \quad i = 1,2,3,... \tag{3}$$

We used a MPI-5 (Poland) microscope which gave an image separation ranging from 4 to 100 μm, depending on the refracting angle of the prism and the objective used. The accu-

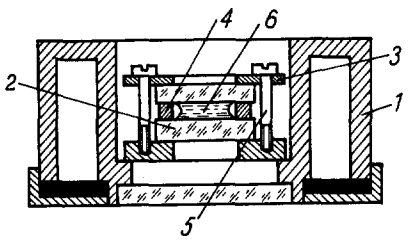

Fig.4 A scheme of a thermally regulated cùvette containing a diffusion cell:
1) thermally regulated jacket
2) glass plates
3) clamps
4) spacers to determine capillary thickness
5) fastening screws
6) sample

racy of measuring the path difference is $\lambda/25$.

This technique allows us to investigate the whole concentration range for polymer - low molecular weight compound systems and polymer - oligomer systems.

The technique is illustrated for the PB - DOP system at 20°C. The molecular mass of PB was 40 000, $M_\omega / M_n = 1.13$, the refraction index of PB $n_2^{20} = 1.5175$ and that of DOP $n_1^{20} = 1.4853$.

The polymer was placed between glass plates which form a flat capillary 100–200 μm thick. The plates were fixed into a cell and the cell placed into a thermally regulated cùvette (Fig.4). After making the temperature uniform the plasticizer was introduced into the capillary to produce an interference pattern, which was photographed at regular intervals (e.g., Fig.3). The data was processed according to equations (1 - 3) and the expression $c_2 = \Delta n/K$, where K is the increment of n. This results in a concentration profile of the polymer $c_2(x)$ in the diffusion zone. Figure 5 shows the results.

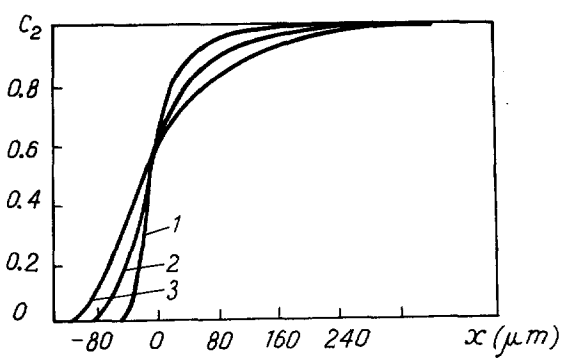

Fig.5 Concentration profiles in the PB - DOP system at 20°C:
1) 4 min
2) 9 min
3) 16 min

The advantages of this technique over the method of optical wedge (1) are its better accuracy (approximately one order of magnitude higher) and the elimination of the need to cover the internal surfaces of the plates with semi-transparent layers of metal or to form a wedge between the plates.

Thus this polarization- interference technique is a convenient and accurate method for studying mutual diffusion over wide concentration ranges and for a variety of systems. It is worth noting that the possibilities of this technique are far from being exhasted.

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