A Modified Optical Schlieren Technique for Measuring the Mutual Diffusion Coefficient in Polymer Blends

M. Ye, R. J. Composto,*,† and R. S. Stein

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: We have developed a modified optical schlieren technique (MOST) for measuring the mutual diffusion coefficient D in miscible polymer blends. A laser light source impinges on the interface of a diffusion couple, and the intensity of refracted rays is detected with an optical multichannel analyzer interfaced with a vidicon detector. The mutual diffusion coefficient is determined by simply measuring the angular deviation of the refracted rays as a function of annealing time. As an experimental test, we measure D at 112 °C for a polystyrene (PS):poly(vinyl methyl ether) blend at 0.35 volume fraction PS. The square of the angle of the maximum deflected rays $\theta_{\max}$ is shown to vary inversely with annealing time. From a plot of $\theta_{\max}{}^2$ versus t^{-1}, the mutual diffusion coefficient is measured, $D = 1.1 \times 10^{-9}$ cm^2/s.

Introduction

Because of the current theoretical interest[1] in understanding the mutual diffusion behavior of polymer melts, scientists have developed sophisticated experimental techniques aimed at overcoming the difficulties associated with polymer diffusion, namely, slow diffusion and low contrast. A complete list of references for these techniques has been compiled by Tirrell.[2] Many of these techniques require either complex instrumentation or inconvenient labeling and, therefore, are not accessible to the typical polymer scientist. In this paper, we present an attractive alternative method, namely, a modified optical schlieren technique (MOST), for measuring mutual diffusion in polymer blends. As we shall show, MOST requires only a simple light scattering apparatus, has straightforward data analysis, and relies on the inherent refractive index difference between polymers for contrast.

The schlieren technique is both simple and straightforward. In 1672, Hooke observed that a ray of light would curve when it passed through a medium with a refractive index gradient, ∇n.[3] While Hooke used a candle to produce a density gradient in the surrounding air, any density gradient in a transparent medium will deflect light such that the magnitude of this deflection is governed by ∇n.[4,5] Hooke's observation provides the basis for the versatile schlieren technique, a technique applicable to a range of problems such as the mutual diffusion of gases and liquids. To our knowledge, this paper is the first attempt to apply this technique to the study of polymer melts. Although the refractive index difference between dissimilar polymers is inherent, the conventional schlieren technique is not optimized to measure the diffusion of macromolecules in a melt because the diffusion distances involved are quite small. By modifying the conventional apparatus and improving data analysis, we have developed a modified optical schlieren technique that can measure mutual diffusion coefficients in polymer blends ranging from 10^{-6} to 10^{-12} cm^2/s.

Schlieren Principles

Recently, several scientists have used the conventional schlieren technique to measure the diffusion of small and large molecules in polymer solutions.[6-8] In these experiments, one observes the familiar bell-shaped schlieren pattern corresponding to a refractive index gradient across the interface of the diffusion couple. Because of the large diffusion distances (on the order of centimeters) and small concentration gradients, mutual diffusion in small-molecule systems can be followed with a conventional schlieren apparatus. This apparatus consists of a mercury lamp and photographic plate for a light source and detection system, respectively. To study melts, the mercury lamp has been replaced with a laser in order to reduce diffraction of the incident beam as it encounters the narrow interfacial region (on the order of microns) associated with polymer-polymer mutual diffusion. Also, instead of measuring the refractive index gradient as in the conventional technique, we measure the deflection of light rays as they pass through the refractive index profile. Defining θ as the angle between the incident rays and those exiting from the back of the sample, the time dependence of θ during interdiffusion yields enough information to allow the determination of the mutual diffusion coefficient. Determining the path of these various rays as they pass through the sample is the subject of the next section.

Regardless of experimental details, the schlieren principle states that a parallel light beam will be deflected by an angle θ as the beam passes through a refractive index gradient ∇n in a transparent medium. For large diffusion distances and small volume fraction (or refractive index) gradients, the path of the deflected rays will be straight as the rays traverse the gradient field and as a result θ is simply related to ∇n.[4,9] However, for polymer melts, the diffusion distances are small and the volume fraction gradients are large. Therefore, a light ray passing through the mixed region between two blends can be curved and as a result θ is no longer simply related to ∇n.[5] In this latter case, the ray path can be followed by the ray-tracing method, which repeatedly applies the law of refraction to "trace" the ray. This method is only valid if the wavelength is small compared to the interfacial thickness (i.e., satisfies geometric optics conditions).[10] In the limit of small θ, the ray-tracing method yields a simple linear relationship between θ and the mutual diffusion coefficient.

Ray-Tracing Method. Figure 1a shows the orientation of the incident laser beam in the y direction with respect to the sample interface. The sample is aligned perpendicular to the incident rays and has a refractive index that varies only along the x direction, $n(x)$. The sample consists of two blends of polymers A and B with volume

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† Present address: Materials and Science and Engineering Department, University of Pennsylvania, Philadelphia, PA 19104.

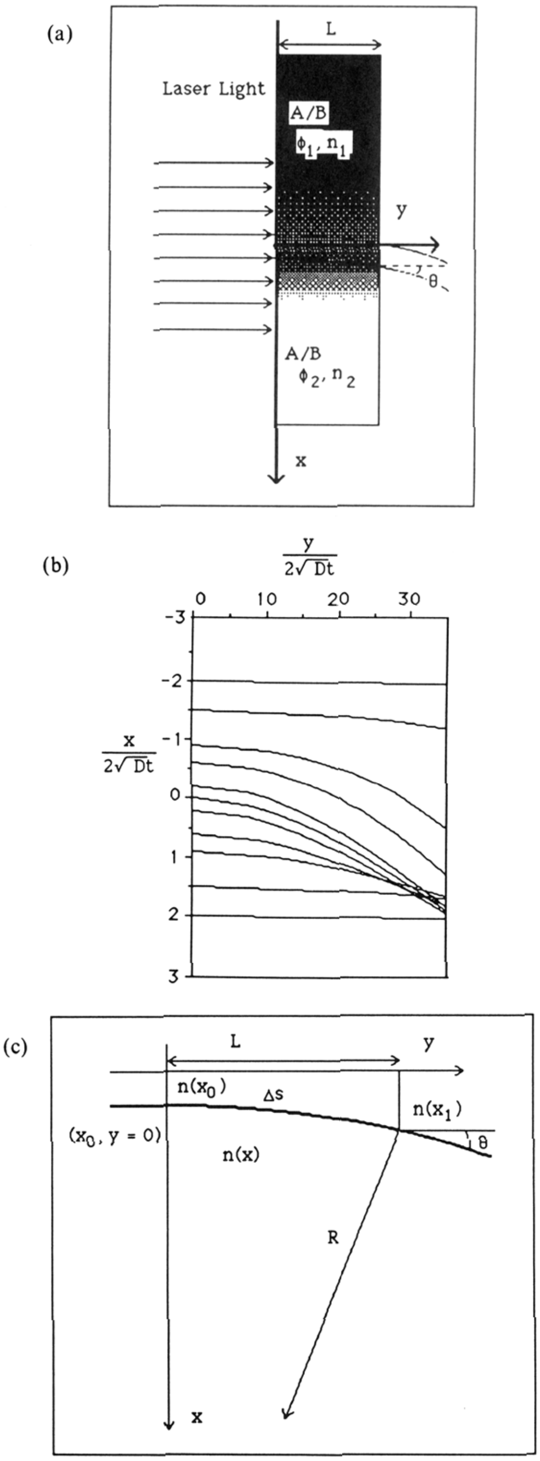

Figure 1. (a) Schematic diagram showing a laser beam incident on an A:B diffusion couple with refractive indices n_1 and n_2. The coordinate system is defined such that the incident light is in the $+y$ direction and the refractive index is a function of x only. (b) Eleven ray trajectories calculated by the ray-tracing method for the case where $(n_1 + n_2)/2 = 1.495$ and $n_2 - n_1 = 0.01$. (c) Geometry used to calculate the relationship between the angle at which the ray leaves the sample and the refractive index gradient in the linear approximation case. The ray enters the sample at coordinates $(x_0, 0)$ and leaves the sample at (x_1, L). The refractive indices upon entering and leaving are $n(x_0)$ and $n(x_1)$, respectively. R is the radius of curvature and Δs the arc length.

fractions of A of ϕ_1 and ϕ_2 or, equivalently, refractive indexes n_1 and n_2. Upon annealing this couple, a mixing region develops at the interface as denoted by the shaded area. If ϕ_1 and ϕ_2 are not very different (e.g., $\phi_1 - \phi_2 = 0.10$), a single mutual diffusion coefficient D should control diffusion,[1] and the composition profile is given by[11]

$$\phi = \phi_1 + \frac{\phi_2 - \phi_1}{2}\left[1 + \operatorname{erf}\left(\frac{x}{2(Dt)^{1/2}}\right)\right] \tag{1}$$

where t is the diffusion time. By analogy, the refractive index profile can be represented as

$$n = n_1 + \frac{n_2 - n_1}{2}\left[1 + \operatorname{erf}\left(\frac{x}{2(Dt)^{1/2}}\right)\right] \tag{2}$$

where n_1 and n_2 were directly measured.[12]

For wavelengths much less than the radius of curvature of the light path, the laser beam can be considered as a bundle of individual rays. Figure 1a schematically defines the angle θ of deflection between the incident ray and the ray leaving the back of the sample. The optical path of the ray can be traced by solving the eiconal diffential equation for the given boundary conditions; i.e., the refractive index is a function of x only and the incident rays are perpendicular to the sample and therefore refract parallel to the x–y plane as shown in Figure 1a.[5] Solutions to the eiconal equation can be found in a variety of scattering books.[5] Here we simply present the results. Using the ray-tracing method, we can describe the trajectory for a ray incident at the coordinate (x_0, $y = 0$) by

$$y = \int_{x_0}^{x-x_0} \frac{n(x_0)}{[n(\xi + x_0)^2 - n(x_0)^2]^{1/2}}\,d\xi, \qquad 0 \le y \le L \tag{3}$$

where $n(x)$ is the refractive index profile, $x = x_0 + \xi$, and L is the sample thickness.[5] Figure 1b shows eleven ray trajectories in the reduced coordinate system $((x/w), (y/w))$, where $w = 2(Dt)^{1/2}$. Parameters inserted into eq 2 to calculate the refractive index profile in this reduced axis were $(n_1 + n_2)/2 = 1.495$ and $n_2 - n_1 = 0.01$. Qualitatively, rays passing through the interfacial region where the refractive index gradient is large are strongly bent toward the $+(x/w)$ direction, whereas rays at the tails of the profile do not deviate appreciably from their initial direction. Note that the rays refract toward the medium with the *highest* refractive index.

If $(x_0, 0)$ and (x_1, L) are the (x, y) coordinates corresponding to a ray entering and exiting the sample as shown in Figure 1c, then the deflection angle can be found by differentiating eq 3 at $y = L$ where

$$\tan\theta = \frac{1}{dy/dx} = \left\{\left[n\left(\frac{x_1}{2(Dt)^{1/2}}\right)\Big/ n\left(\frac{x_0}{2(Dt)^{1/2}}\right)\right]^2 - 1\right\}^{1/2} \tag{4}$$

Because x_1 is related to the sample thickness by eq 3, namely

$$\frac{L}{2(Dt)^{1/2}} = \int_{x_0/2(Dt)^{1/2}}^{x_1/2(Dt)^{1/2}} \frac{n\left(\dfrac{x_0}{2(Dt)^{1/2}}\right)}{n(\xi)^2 - n\left(\dfrac{x_0}{2(Dt)^{1/2}}\right)^2}\,d\xi \tag{5}$$

the diffusion coeficient can be evaluated by plotting the square of the deflected angle as a function of t^{-1} and fitting the data with eqs 4 and 5. This data analysis will be referred to as the *ray-tracing method* in the duration of the paper.

Linear Approximation. As shown in Figure 1c, the angle θ is related to the radius R of the curved ray by

$$\theta = \Delta s/R \tag{6}$$

where Δs is the curve length between $(x_0, 0)$ and (x_1, L).

From simple geometry, the radius is defined as

$$R = \left| \frac{[1 + (\mathrm{d}y/\mathrm{d}x)^2]^{3/2}}{\mathrm{d}^2y/\mathrm{d}x^2} \right| \tag{7}$$

Assuming that $n(x_0) \approx \tilde{n} = (n_1 + n_2)/2$ and $\Delta s \approx L$, eqs 3, 6, and 7 can be combined to give the deflection angle of a ray:

$$\theta = \frac{L}{\tilde{n}} \frac{\mathrm{d}n}{\mathrm{d}x} \tag{8}$$

Substituting eq 2 into eq 8, the deflection angle of rays passing through the refractive index gradient is given by

$$\theta = \frac{L}{\tilde{n}} \frac{\Delta n}{2(\pi D t)^{1/2}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{9a}$$

with the maximum angle $\theta_{\max}$ corresponding to rays incident on the maximum refractive index gradient (i.e., at $x = 0$)

$$\theta_{\max} = \frac{L}{\tilde{n}} \frac{\Delta n}{2(\pi D t)^{1/2}} \tag{9b}$$

Thus eq 9b predicts that a plot of $\theta_{\max}^2$ versus t^{-1} should yield a straight line with a slope that is inversely proportional to the mutual diffusion coefficient. Note that eq 9b is only valid in the small-angle limit (see Figure 1c).

Experimental Procedure

Sample Preparation. To measure mutual diffusion coefficients in blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME), diffusion couples were made that consisted of two blends of PS:PVME with PS volume fractions of ϕ_1 and ϕ_2, respectively. Samples were prepared by weighing PS(ϕ_1) and PVME solids, dissolving the solids in toluene, and drying this mixture in a fume hood and vacuum oven. The resulting PS(ϕ_1):PVME blend was then placed in a brass mold (1 cm × 1 cm × L) and hot pressed at a temperature 80 °C greater than the glass transition temperature of the blend. The sample thickness L ranged from 100 to 500 μm. A similar procedure was used to create the second slab of PS(ϕ_2):PVME. A sharp interface was established between the two PS:PVME slabs by butting the blocks together and then clamping the sample between two cover glass slides separated by a metal spacer of thickness L.

One advantage of the PS:PVME system is that blends rich in PVME are rubbery at room temperature (i.e., $T_g < T_{\mathrm{rm}}$), and therefore the joining of the two layers can be carried out at T_{rm}. Another useful characteristic is the large difference in refractive index between PS ($n = 1.585$) and PVME ($n = 1.466$) at T_{rm}.[12] For a system with a small Δn, the sensitivity of the experiment can be increased by simply increasing the sample thickness (i.e., $\theta_{\max}^2 \propto L\Delta n$). Following preparation, the diffusion couple was heated on a programmable Koefler hot stage, mounted on the optical bench shown in Figure 2.

Apparatus. All measurements were performed on an optical multichannel analyzer apparatus (OMA3) in a one-dimensional scanning mode. Details of this optical multichannel analyzer apparatus have been published elsewhere.[13] A schematic diagram of this apparatus is given in Figure 2. Light rays from a helium–neon laser of wavelength 632 nm impinge on the interface of a diffusion couple and enter the sample. Those rays incident on the refractive index gradient are refracted whereas rays not incident on the gradient pass straight through the sample undeflected. After the rays pass through the sample, a series of three lenses focus the deflected (thick line) and undeflected rays (thin lines) onto a silicon-intensified vidicon detector. A scan of the intensity as a function of angle θ requires about 10^{-2} s, which is much less than our diffusion times. Usually 50–80 such scans are accumulated during the annealing of the couple.

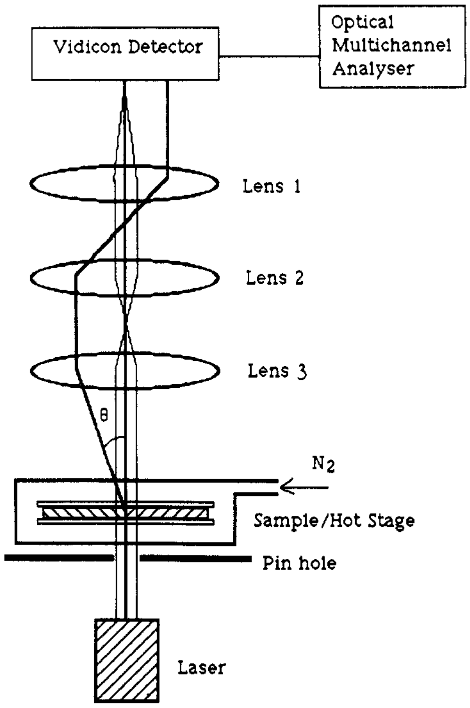

Figure 2. Geometry of the modified schlieren apparatus with the laser light source and vidicon detector system. The thick line represents the path of ray passing through a refractive index gradient in the sample, while the thinner lines represent undeflected rays.

Results

Selected MOST scans of intensity versus angle are shown in Figure 3 for a PS:PVME couple at 112 °C. The weight-average molecular weights of the PS and PVME are 2950 and 99 000, respectively, and the volume fractions of PS in the two blends are $\phi_1 = 0.3$ and $\phi_2 = 0.4$. Note that the peak at $\theta = 0°$ corresponds to the rays that are not deflected. Those rays that pass through the refractive index gradient exit the back of the sample at various angles and as a result interfere with each other. This interference gives rise to the intensity maxima and minima shown in Figure 3. As denoted by the arrows, the intensity maxima at the largest angle $\theta_{\max}$ decrease as the annealing time increases, in qualitative agreement with eq 9b. For example, after 3.3 h, $\theta_{\max}$ is located at 1.85°, whereas upon further annealing, $\theta_{\max}$ moves to 1.35° and 0.92° after 6.4 and 12.6 h, respectively.

Figure 4 shows a plot of $\theta_{\max}^2$ versus t^{-1} for the experiment discussed in Figure 3. The angles $\theta_{\max}$ denoted by arrows in Figure 4 correspond to the arrows shown in Figure 3. As predicted by eq 9b, a linear relationship is indeed realized because of the small angles involved in this experiment. Thus, data analysis by the linear approximation method can be used to extract the mutual diffusion coefficient. In general, for diffusion coefficients greater than 10^{-9} cm^2/s the linear approximation can be used, whereas for small diffusion coefficients the ray-tracing method is necessary. Using eq 9b, we calculate a mutual diffusion coefficient from the slope of the plot in Figure 4 using the blend refractive indexes of $n_1 = 1.478$ and $n_2 = 1.489$ and a sample thickness of 0.518 mm.[12] Applying a least-squares fit to the data (solid line), we find that the mutual diffusion coefficient for a PS:PVME blend at 112 °C and PS volume fraction of 0.35 is 1.1×10^{-9} cm^2/s. As expected, the more accurate ray-tracing method yields an identical value of D.

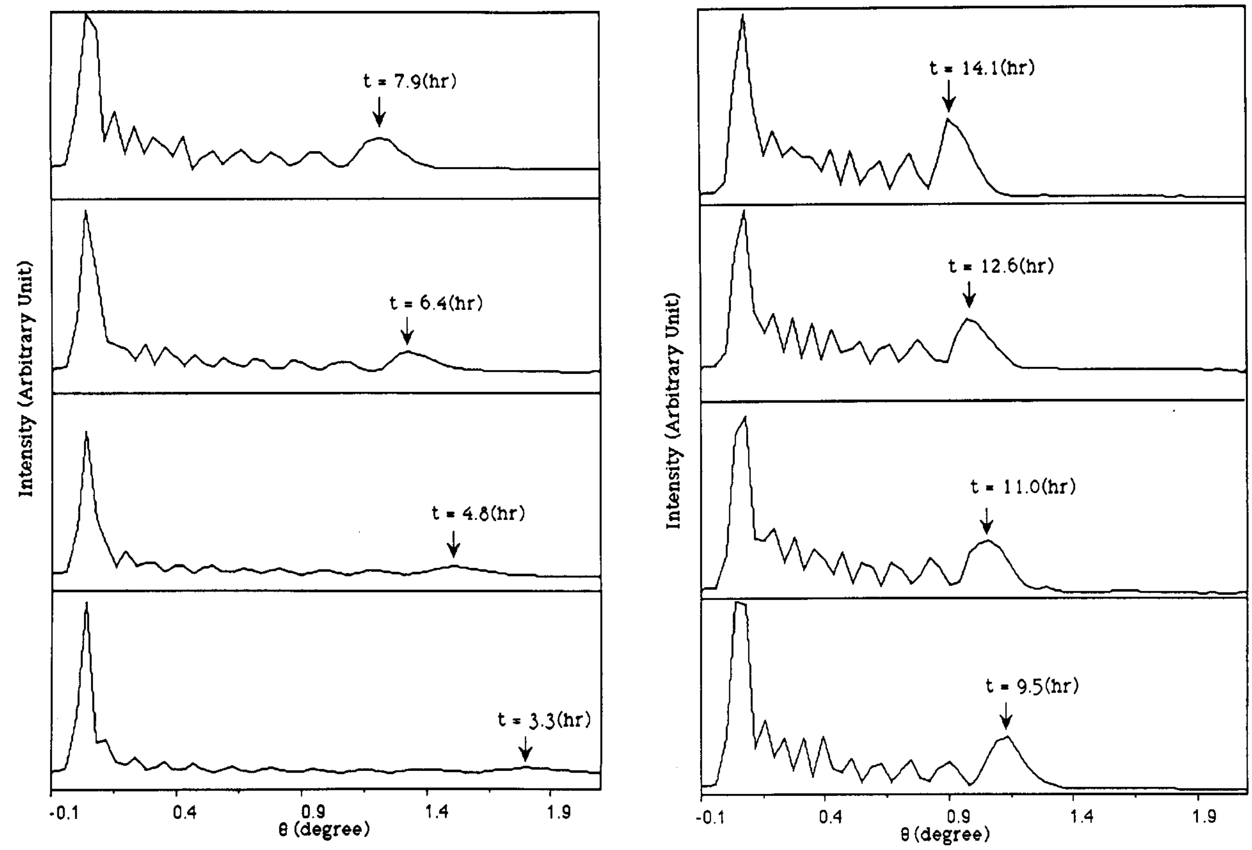

Figure 3. Arbitrary intensity versus deflected angle plots at 112 °C for diffusion times of 3.3, 4.8, 6.4, 7.9, 9.5, 11.0, 12.6, and 14.1 h. The sample is a PVME (M_w = 99 000):PS (M_w = 2950) diffusion couple with an average volume fraction of PS of 35%. The arrows follow the decrease of θ_{max} with increasing time.

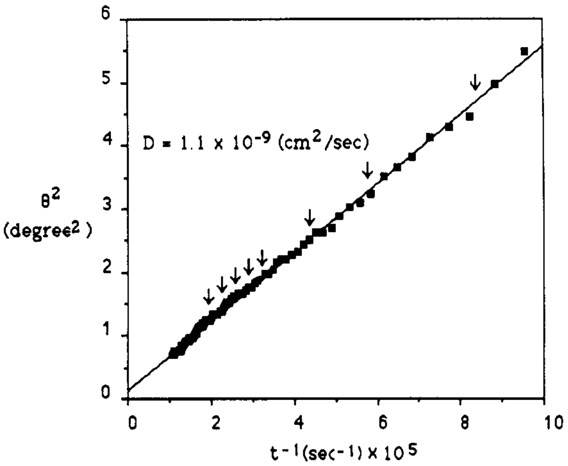

Figure 4. A plot of θ_{max}^2 versus t^{-1} for the sample described in Figure 3. The arrows show the values of θ_{max} determined from Figure 3. The solid line is a least-squares fit to the data, and the slope of this line yields a diffusion coefficient of 1.1 × 10^{-9} cm²/s.

Discussion

The main limitation of the modified schlieren technique results from the diffraction of the incident rays as the laser beam encounters a sharp interface. The analysis methods presented are valid only when the wavelength of the incident beam is small compared to the diffusion distance, $\lambda \ll \Delta x$. The wavelength of a He–Ne laser is 0.623 μm, and, therefore, to avoid diffraction problems, diffusion distances greater than this are necessary. Simulations show that diffraction of the laser is appreciable up to a diffusion distance of 10 μm.[12] Letting $\Delta x \sim (Dt)^{1/2}$, diffusion coefficients ranging from 10^{-6} to 10^{-12} cm²/s can be measured by MOST with experimental annealing times of several hours to several days, respectively.

The main sources of experimental error in determining D are (1) the errors in measuring θ_{max}, the sample thickness, and the refractive index, (2) the roughness of the initial interface of the diffusion couple, and (3) the interference between the main beam and deflected rays. The relative error of the diffusion coefficient is the sum of the individual relative errors[14]

$$\frac{\Delta D}{D} = \frac{\Delta L}{L} + \frac{\Delta(\Delta n)}{\Delta n} + \frac{\Delta \theta}{\theta} + \frac{\Delta t}{t} \qquad (10)$$

The error in measuring the sample thickness L and refractive index difference Δn is ca. 5% for both errors. The uncertainty in θ_{max} depends on the diffraction effects discussed previously and can be set to 10%. Because each scan was accumulated in much less than a second, the error introduced by measuring the intensity as a function of angle during diffusion is negligible. However, the relative error of time can be large because of the uncertainty of the initial diffusion time, t_0. Ideally, when two slabs of polymer are joined together, a sharp boundary is created at the interface and the diffusion time at that moment can be set to zero. However, roughness at the interface will smear the initial interface and introduce a relative error ($\Delta t_0/t_0$) given by

$$\frac{\Delta t_0}{t_0} = \frac{\sigma^2}{D t_0} \qquad (11)$$

where σ is the initial roughness. As observed in Figure 4, the uncertainty in t_0 manifests itself as a finite value of θ_{max} as t goes to infinity. If σ is on the order of 1 μm, the error introduced by $\Delta t_0/t_0$ increases dramatically as the diffusion coefficient decreases. Combining all errors, the total relative error of $\Delta D/D$ is ca. 20% + $\Delta t/t$, where $\Delta t/t$ can be as large as 50% for $D = 10^{-12}$ cm²/s.

While many studies of the thermodynamics of polystyrene:poly(vinyl methyl ether) blends exist, measurements of the mutual diffusion coefficient in PS:PVME are sparse.[15-17] Because of this lack of data, we are currently measuring D by forward recoil spectrometry,[18] a proven experimental technique, so as to test the accuracy of MOST. A future publication will contain these results.

Conclusion

In this paper, we present an old technique with a new twist. By simple modifications of the conventional schlieren apparatus, a modified optical schlieren technique (MOST) was shown to be capable of measuring mutual diffusion coefficients in polymer blends. The current range of measurable diffusion coefficients is 10^{-6}–10^{-12} cm^2/s. Because the refractive indexes of polymers are inherently different, MOST can be applied to a wide variety of polymer blends without the necessity of labeling one or both of the polymers to provide contrast. This convenience not only simplifies sample preparation but also eliminates any change in the nature of the system. At low angles, the angles of the deflected rays is related to the mutual diffusion coefficient by a very simple equation, $\theta_{\max}{}^2 \propto 1/(Dt)$. In the experiment discussed here, this linear relationship is indeed realized as shown in Figure 4. For slow diffusion (or at short times), the rays will be strongly bent and as a result a simple relationship between $\theta_{\max}$ and D will no longer exist. In this case either one can wait until $\theta_{\max}$ becomes small enough to apply the linear approximation or one can apply the ray-tracing method to analyze the data and in turn measure the mutual diffusion coefficient. In the current data analysis, only $\theta_{\max}$ is used to determine D. To further improve this technique, complete curve fitting of the intensity versus angle spectrum should be applied so as to shorten the experimental time, improve the precision of D, and extend the measurable range of diffusion coefficients.

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