

The mutual diffusion coefficient for (meth)acrylate monomers as determined with a nuclear microprobe

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(Received 15 September 2003; accepted 29 October 2003)

The value of the mutual diffusion coefficient D^V of two acrylic monomers is determined with Nuclear Microprobe measurements on a set of polymer films. These films have been prepared by allowing the monomers to diffuse into each other for a certain time and subsequently applying fast ultraviolet (UV) photo-polymerization, which freezes the concentration profile. The monomer diffusion profiles are studied with a scanning 2.1 MeV proton microprobe. Each monomer contains a marker element, e.g., Cl and Si, which are easily detected with proton induced x-ray emission (PIXE). From the diffusion profiles, it is possible to determine the mutual diffusion coefficient. The mutual diffusion coefficient is dependent of concentration, which is concluded from the asymmetry in the Cl- and Si-profiles. A linear dependence of the mutual diffusion coefficient on the composition is used as a first order approximation. The best fits are obtained for a value of $b = (0.38 \pm 0.15)$, which is the ratio of the diffusion coefficient of 1,3-bis(3-methacryloxypropyl)-1,1,3,3-tetramethyldisiloxane in pure 2-chloroethyl acrylate and the diffusion coefficient of 2-chloroethyl acrylate in pure 1,3-bis(3-methacryloxypropyl)-1,1,3,3-tetramethyldisiloxane. Under the assumption of a linear dependence of the mutual diffusion coefficient D^V on monomer composition, it follows that $D^V = (2.9 \pm 0.6) \cdot 10^{-10} \text{ m}^2/\text{s}$ at a 1:1 monomer ratio. With Flory-Huggins expressions for the monomer chemical potentials, one can derive approximate values for the individual monomer diffusion coefficients. © 2004 American Institute of Physics.

[DOI: 10.1063/1.1635800]

INTRODUCTION

Optical applications for polymer films and coatings are found in data transport,^{1,2} storage³ and displays. For many of these layers, it is essential that they have some sort of distribution in either refractive index, film thickness or surface profile. Holographic and lithographic UV illumination are techniques used to prepare polymer structures having a modulation in monomer unit concentration from a homogeneous mixture of two monomers. By applying a modulation in the light intensity, polymerization is started in the regions that are illuminated by UV light, while in nonilluminated regions no reaction occurs.⁴ A difference in reactivity and other monomer properties such as molecular size, monomer-monomer and monomer-polymer interaction, leads to gradients in the monomer chemical potentials. These gradients in the monomer chemical potential induce monomer migration during the polymerization process and result in lateral differences in monomer-unit concentration of the final polymer structure. If two monomers with an intrinsic difference in

refractive index are used, these concentration modulations directly correspond to a modulation of the refractive index.

In previous articles,^{5,6} nuclear microprobe measurements on lithographically prepared gratings prepared from two monomers were presented. Because each monomer contains a different marker element, i.e., Cl, F, or Si, independent measurement of the monomer units in the polymer films is possible. Sometimes both monomers migrate towards the illuminated regions and sometimes one monomer migrates towards the illuminated regions while the other migrates towards the dark regions. A model has been developed to describe this monomer reaction-diffusion process of these gratings. The results of the model will be compared with the nuclear microprobe measurements and will be published elsewhere.

In order to model the reaction/diffusion mechanism of the grating preparation process, it is necessary to determine the diffusion coefficients of the monomers, independently. Although the diffusion coefficients of these monomers decrease drastically as a function of monomer conversion, the values of the diffusion coefficients at low conversions are the

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most important, since these are the highest and dominate the overall reaction–diffusion mechanism. In this article, a convenient method is described to determine the mutual diffusion coefficient of two monomers, where two pure monomers are made to diffuse into each other and are analyzed on their position dependent concentration in time. Thereto two liquid films of mutually different monomers were transported towards each other in the gap between two spaced glass plates under the action of capillary forces. As soon as they touched, the time was set at zero, and diffusion of the two monomers into each other's bulk took place. After a certain time t the diffusion was stopped by a photo-initiated polymerization/crosslinking reaction under high intensity irradiation and the concentration profile is fixed. The polymerization proceeds very fast on the time scale of diffusion. The concentration profiles could be analyzed by nuclear microprobe measurements.

The Flory–Huggins theory is used to obtain the diffusion equations with chemical potentials, instead of concentrations, as the driving force for diffusion.⁷ In this way, diffusion is not only driven by a difference in monomer concentration but also by entropic size effects, which may play a role since these monomers here are not globular.

THEORY

During preparation of a grating by patterned UV photo-polymerization⁵ from a mixture of two monomers, the system contains an illuminated and a dark region. Three components have to be considered in the UV illuminated regions, i.e., the two monomers and the polymer.^{5,6}

However, for the diffusion experiments discussed in this article, one starts with two pure liquid monomers touching each other at a certain position. Therefore, the polymer phase needs not be considered, since all diffusion takes place when the monomers are still liquid. And, for simplicity, the Flory–Huggins interaction parameters χ are assumed to be zero. The chemical potentials μ_1 and μ_2 of the two monomers 1 and 2 are given by the Flory–Huggins expressions^{8,9}

$$\mu_i - \mu_i^0 = kT \left(\ln \varphi_i + 1 - \varphi_i - \frac{v_i}{v_j} \varphi_j \right) \quad \text{for } (i,j) = (1,2), (2,1). \quad (1)$$

Here, μ_1^0 and μ_2^0 are the chemical potentials of the unmixed phases of monomer 1 and 2 respectively, φ_1 , φ_2 are the volume fraction of monomer 1, and monomer 2. The number of segments of the two monomers and the polymer, as defined in the Flory–Huggins model, is given by v_1 and v_2 , respectively. Interestingly, since the number of segments is directly related to the size or length of the monomer, there is a length or size dependent factor v_1/v_2 . This factor is sometimes called size entropy¹⁰ and plays a role for oblong molecules with different lengths. The one-dimensional diffusion of monomer i is described by the more general thermodynamic treatment of the diffusion equations

$$\frac{\partial \varphi_i}{\partial t} = \frac{\partial}{\partial x} \left(\frac{D_i \varphi_i}{kT} \frac{\partial \mu_i}{\partial x} \right). \quad (2)$$

Here, the total volume is constant for all positions x , D_i is the diffusion coefficient, μ_i the local chemical potential and φ_i the local volume fraction of monomer i . With $\varphi_2 = 1 - \varphi_1$ and carrying out the differentiation of μ_i to φ_i

$$\frac{\partial \varphi_i}{\partial t} = \frac{\partial}{\partial x} \left(D_i^{\text{eff}}(\varphi_1) \frac{\partial \varphi_i}{\partial x} \right)$$

with

$$D_i^{\text{eff}} = D_i \left(1 + \varphi_i \left(\frac{v_i}{v_j} - 1 \right) \right) \quad \text{for } (i,j) = (1,2), (2,1). \quad (3)$$

Thus, in the case that there is no polymer, the diffusion equation reduces to a situation where the diffusion is given by two effective intrinsic diffusion coefficients D_i^{eff} that are both functions of φ_1 since $\varphi_2 = 1 - \varphi_1$.

If the diffusing species are both liquids, there is no net volume transport and the diffusion is described by intrinsic diffusion of each monomer plus transfer of total volume by bulk-flow.¹¹ Any excessive migration of one monomer is compensated by this bulk-flow, and the total volume remains constant for all x . Using a constant overall volume, one can derive that the mutual diffusion coefficient D^V at a certain value of φ_1 is a linear combination of the two effective intrinsic monomer diffusion coefficients at φ_1 .¹¹

$$D^V(\varphi_1) = \varphi_1(D_2^{\text{eff}}(\varphi_1) - D_1^{\text{eff}}(\varphi_1)) + D_1^{\text{eff}}(\varphi_1). \quad (4)$$

So, D^V is a function of φ_1 , D_1 , and D_2 . For the monomers considered here, it is not expected that the order of magnitude of the two diffusion coefficients will be different. As a first-order approximation, D^V is, therefore, assumed to be a linear function of φ_1 , with D_1^0 and D_2^0 the values for $\varphi_1 = 0$ and $\varphi_1 = 1$, respectively,

$$D^V(\varphi_1) = \varphi_1(D_2^0 - D_1^0) + D_1^0, \quad (5)$$

D_1^0 and D_2^0 correspond to the values of $D_1^{\text{eff}}(0) = D_1(0)$ and $D_2^{\text{eff}}(1) = D_2(1)$, respectively, as is verified with Eqs. (3) and (4). If the difference in D_1 and D_2 is large, such a linear approximation may become too inaccurate.

The diffusion of the two-monomer system can thus be described by Fick's second law with a mutual diffusion coefficient D^V that is a function of φ_1

$$\frac{\partial \varphi_i}{\partial t} = \frac{\partial}{\partial x} \left(D^V(\varphi_1) \frac{\partial \varphi_i}{\partial x} \right) \quad \text{for } i = 1,2. \quad (6)$$

The situation considered here starts with one pure monomer on either side of $x=0$. The boundary conditions and initial conditions for $\varphi_1(x,t) = 1 - \varphi_2(x,t)$ are given by

$$\begin{aligned} \varphi_1(-\infty, t) = 1 & \quad \varphi_1(x, 0) = 1 & \quad \text{for } x < 0, \\ \varphi_1(\infty, t) = 0 & \quad \varphi_1(x, 0) = 0 & \quad \text{for } x > 0, \\ \varphi_1(0, 0) = \frac{1}{2}. \end{aligned} \quad (7)$$

If the mutual diffusion coefficient D^V is a constant, i.e., not a function of φ_1 , the general solution for Eq. (6), with boundary conditions given by Eq. (7), is given by an error function profile for $\varphi_1(x,t)$, as can be found in any book about differential equations

$$\varphi_1(x,t) = \frac{1}{2} \left(1 - \operatorname{erf} \left[\frac{x}{2\sqrt{D^V t}} \right] \right). \quad (8)$$

Here, the x -coordinate is defined with respect to the position where $\varphi_1 = \varphi_2 = 0.5$, and t is the diffusion time. This is the point where the liquids touched initially. The faster intrinsic diffusion of one monomer in one direction is exactly compensated by bulk flow to the opposite direction in order to keep the volume constant for all x . The result is that the diffusion profile remains symmetric with respect to $x=0$, which means that the position of $\varphi_1 = 0.5$ does not move itself during the diffusion process.¹¹

If it is assumed that the mutual diffusion coefficient D^V is not a constant and depends linearly on the volume fraction φ_1 , as in Eq. (5), there is no analytical solution of Eq. (6) for $\varphi_1(x,t)$. The solution is then an asymmetric modified error function profile and this function f is not only a function of $x/2\sqrt{D_a t}$ but also of a parameter b .^{11,12}

$$\varphi_1(x,t) = f \left(\frac{x}{2\sqrt{D_a t}}, b \right). \quad (9)$$

Here, x is again the distance to the position where both monomer fractions equaled 0.5 at $t=0$. Further, D_a is the mutual diffusion coefficient for $\varphi_1 = 0.5$, and t is the diffusion time. The parameters D_a and b are related to D^V , D_1^0 , and D_2^0 in the following way:

$$D_a = \frac{D_2^0 + D_1^0}{2}, \quad (10)$$

$$b = \frac{D_2^0}{D_1^0}, \quad (11)$$

$$D^V = \varphi_1(D_2^0 - D_1^0) + D_1^0. \quad (12)$$

For $b=1$, D^V becomes constant again as verified with Eqs. (11) and (12). The function given by Eq. (9) reduces to the standard error function of Eq. (8). For other values of b , the solution for φ_1 is given by Eq. (9) and is presented by a table of φ_1 as a function of $x/2\sqrt{D_a t}$ for different values of b .^{11,12}

Related to the fact that D^V depends on φ_1 , the volume fraction profile is asymmetric, and the position where $\varphi_1 = 0.5$ moves in time towards the side where the mutual diffusion coefficient is lowest. Although we have to present diffusion profiles and the magnitudes of D^V first, we notify that the relation between the mutual diffusion coefficient and the two intrinsic diffusion coefficients of the two monomers is summarized graphically in Fig. 1.

In the case of a linear molecule, it has been shown⁸ that, the friction of a molecule is proportional to its length and the diffusion coefficient is inversely proportional to its length, i.e., $D_1 = (v_2/v_1)D_2$. It can be shown that in this particular case

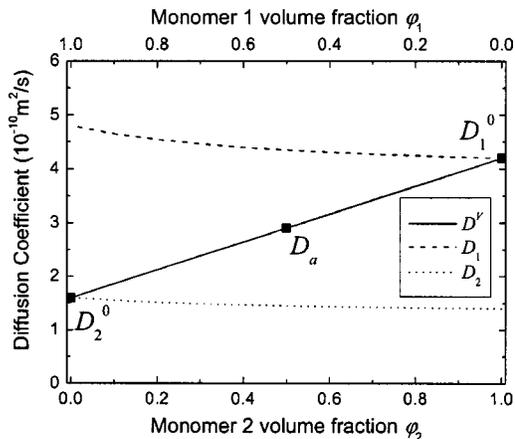


FIG. 1. The mutual (D^V) and individual diffusion coefficients of monomer 1 (D_1) and monomer 2 (D_2) as a function of the composition, $\varphi_1 = 1 - \varphi_2$, assuming the mutual diffusion coefficient to be a linear function of the composition. The dashed and dotted lines have been reconstructed with Eq. (13).

$$\begin{aligned} D^V(\varphi_1) &= D_1^{\text{eff}}(\varphi_1) \\ &= D_2^{\text{eff}}(\varphi_1) \\ &= D_1(\varphi_1) \left(1 + \varphi_1 \left(\frac{v_1}{v_2} - 1 \right) \right) \\ &= D_2(\varphi_1) \left(1 + \varphi_2 \left(\frac{v_2}{v_1} - 1 \right) \right). \end{aligned} \quad (13)$$

Consequently, the intrinsic diffusion coefficients $D_1(\varphi_1)$ and $D_2(\varphi_1)$ can be determined from the mutual diffusion coefficient as a function of φ_1 .

EXPERIMENT

Samples for the determination of the mutual diffusion coefficient for a 2-chloroethylacrylate (Cl-monoacrylate) and 1,3-bis(3-methacryloxypropyl)-1,1,3,3-tetramethyldisiloxane (Si-dimethacrylate) system were prepared in the following way. About 1 mass percent of hexanedioldiacrylate was added to the Cl-monoacrylate in order to create slightly crosslinked polymer film during polymerization enabling handling of the film for analysis. It is assumed that this has no significant effect on the diffusion coefficients. About 2 mass percent of photo-initiator Irgacure 651 was added to both monomers. A cell of two glass slides was filled with Cl-monoacrylate (monomer 1) from one side and with Si-dimethacrylate (monomer 2) from the other side. The UV-light source was placed at a distance of less than one centimeter to the cell. After the two liquids had touched, the monomers were allowed to diffuse into each other for a certain time t . Then, the UV light source was switched on, which led to a fast polymerization, due to the high photo-initiator concentration and the short UV light source distance. Finally, the film was peeled off the glass slides. The whole procedure was done for $t = 10$ s, 20 s, 2 min, 6.5 min, 12 min, and 1 hour and six polymer films were obtained with a thickness of about 20 μm .

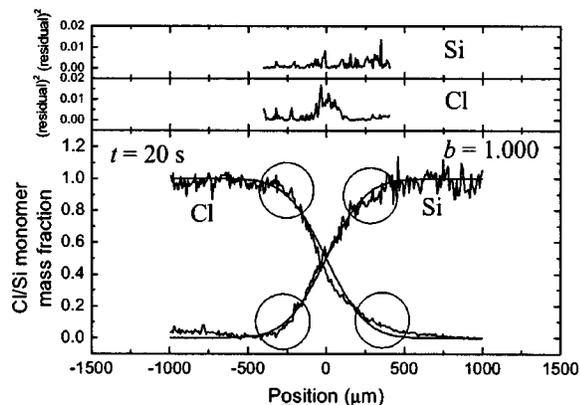


FIG. 2. The diffusion profile after 20 s. The fit is obtained with a value of $b=1.000$ which corresponds to a constant mutual diffusion coefficient, i.e., independent of φ_1 . This profile is described by an error function profile, which is symmetric with respect to the line $x=0$. The squared residual of the least-squares fit is shown in the top graph.

These polymer films were then analyzed with the NUS nuclear microprobe¹³ on a Singletron accelerator at a proton energy of 2.1 MeV. The resolution of the scanning proton beam was about $2 \mu\text{m}$. To avoid severe irradiation damage, a current of typically 10 pA and an integrated charge of 12 nC was used on a total scan area of about 1×1 or $2 \times 2 \text{ mm}^2$, after which the data was summed in one dimension. The Si-dimethacrylate and Cl-monoacrylate monomer mass fraction as a function of position were determined from the Si- and Cl-PIXE yields. Because the film was prepared from a fixed liquid film, the film thickness is constant. A calculation of the variations in x-ray attenuation due to the nonuniform composition shows that there will be a slight error in the diffusion profiles. This error in the monomer mass fraction is only 0.02 for Si and 0.01 for Cl at the positions where $\varphi_1=0.1$ and $\varphi_2=0.1$, and reaches a maximum of 0.04 for Si and 0.03 for Cl at the position where $\varphi_1=\varphi_2=0.5$. Both yields were therefore only corrected for the background signal in the spectrum and were then normalized on the yield of a region of the film that consists of only one component. These normalized yields could then directly be translated to the monomer mass fractions.

RESULTS AND DISCUSSION

Figure 2 shows the Cl- and Si-profiles for $t=20 \text{ s}$. It is seen that the Si- and Cl-contours are not symmetric. The slopes of the measured data are steeper for negative than for positive x -values. Assuming a constant D^V , i.e., independent of φ_1 , a least squares fit was made of the Cl and Si profiles with an error function [Eq. (8)] with two fitting parameters: $D^V t$ and the position of $x=0$. The latter is included because the origin of the x axis is arbitrary at first. The contours could however not be fitted accurately enough as seen in Fig. 2. For positive x -values, the fit is too steep compared to the measured data, as seen in the encircled regions on the right. For negative x -values, the fit is too gradual, as seen in the encircled regions on the left. This phenomenon was most clearly observed for the profiles at 10 s, 20 s, and 2 min. The deviations are larger than any error caused by composition

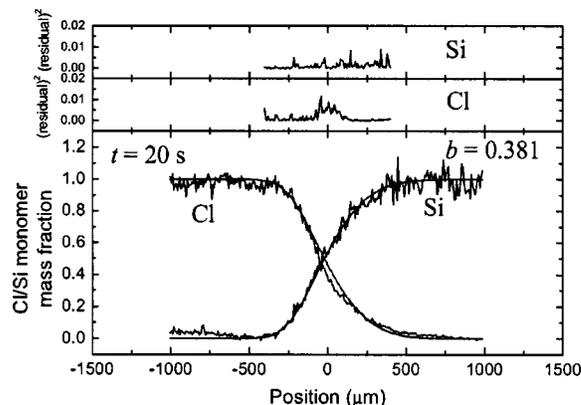


FIG. 3. The diffusion profile after 20 s. The fit is obtained with a value of $b=0.381$ which corresponds to a mutual diffusion coefficient that depends linearly on φ_1 . The fit is asymmetric with respect to the line $x=0$. The position at which $\varphi_1=\varphi_2=0.5$ is on the left side of $x=0$. The squared residual of the least-squares fit is shown in the top graph.

dependent variations in x-ray attenuation. A constant value of D^V , i.e., independent on φ_1 is, therefore, rejected.

If it is assumed that the mutual diffusion coefficient depends linearly on the volume fraction of the monomers in the monomer mixture and that the intrinsic diffusion coefficient scales with the length of the monomers, the values of the individual diffusion coefficients can be determined. When assuming a linear relationship between the mutual diffusion coefficient and the monomer volume fraction, as described by Eq. (5), the measured profiles could be fitted as seen in Fig. 3. A least squares fit with three fitting parameters, i.e., b , $D_a t$ and the position of $x=0$, was made. The fit is better than for the constant D^V , as shown by comparing Figs. 2 and 3 and looking at the residuals. In this way, three optimal values of b were found from the curves at 10 s, 20 s, and 2 min. Only these three curves were used because only here the entire diffusion profile was measured. The average of these values was $b=0.38 \pm 0.15$, which accounts for an asymmetric diffusion profile.

With this value of b now for all six measurements, a value of $D_a t$ was determined for each of the six measurements from a least squares fit of the Si- and Cl-profiles with Eq. (9), now with only $D_a t$ and the position of $x=0$ as fitting parameters. These fits are displayed in Fig. 4. It is clearly seen that both the Si- and the Cl-profiles become less steep for larger diffusion times, i.e., the monomers diffuse deeper into each other. A graph of the obtained values of $D_a t$ versus t was made in order to determine the slope D_a as shown in Fig. 5. When the UV-light is switched on, it still takes some time before the diffusion is sufficiently stopped due to polymerization. Therefore, the curve does not intersect the horizontal axis at $t=0$ but at $t=-t^*$. The effective diffusion time is given by $t_{\text{eff}}=t+t^*$, where t^* is the time between switching on the UV light source and the end of the diffusion process. It is reminded that t is only the time between the touching of the liquids and the point of switching on the UV light source.

From this graph, both the mutual diffusion coefficient and t^* were determined: $D_a=(2.9 \pm 0.6) \cdot 10^{-10} \text{ m}^2/\text{s}$ and t^* was about 35 s. The order of magnitude of t^* is in accor-

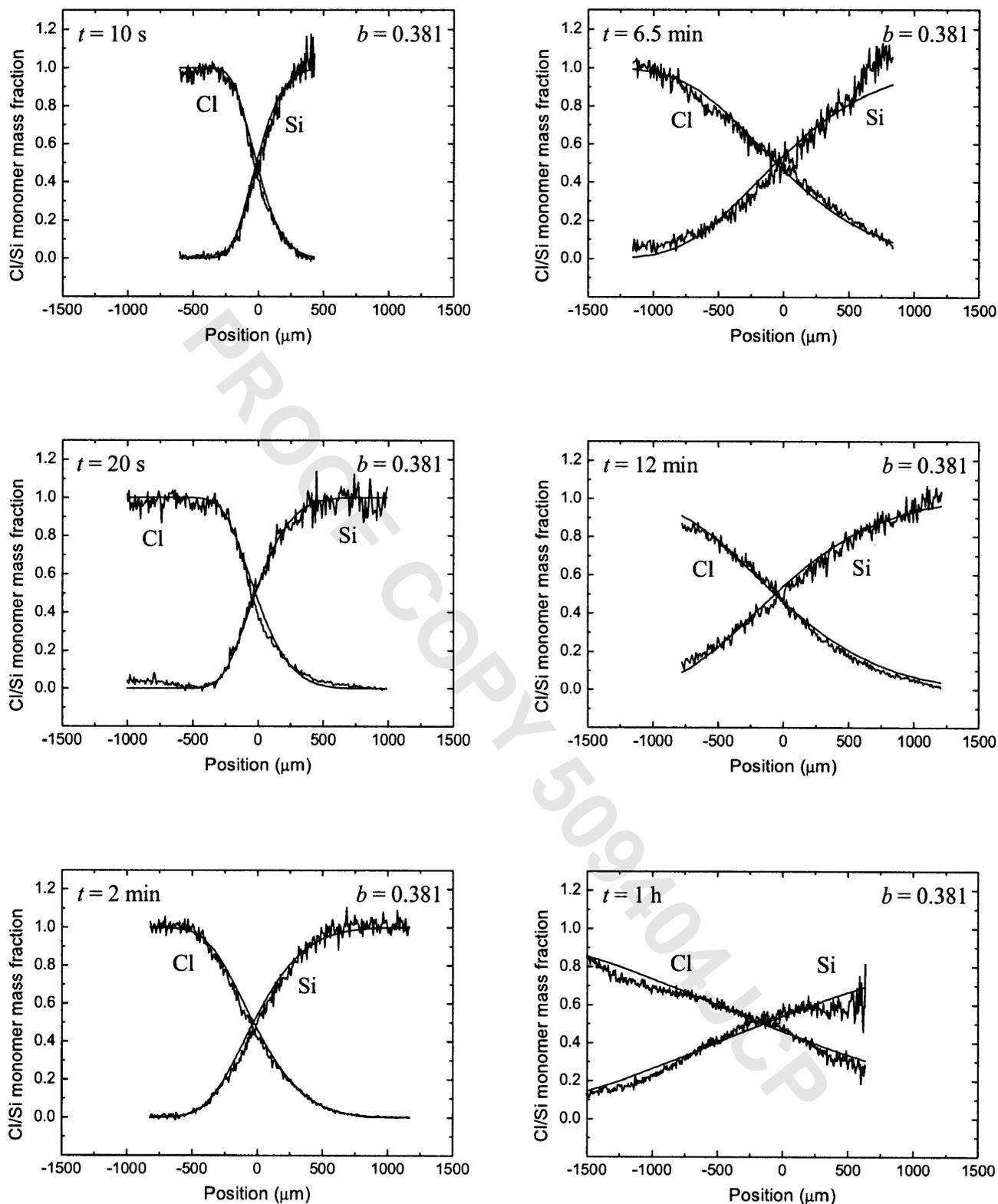


FIG. 4. The diffusion profiles for different values of the time: $t=10$ s, 20 s, 2 min, 6.5 min, 12 min, and 1 h. All fits are obtained with a value of $b=0.381$.

dance with the typical time it takes to polymerize the film. D^V , D_1^0 , and D_2^0 were then determined from D_a and b with Eqs. (10)–(12) and are represented in Fig. 1. The suggested values of $D_1(\varphi_1)$ and $D_2(\varphi_1)$ are calculated from Eq. (13) and are represented by a dashed and dotted line in Fig. 1, respectively. The larger linear Si-dimethacrylate is treated as

a molecule of relative length $v_2=3$ whereas the Cl-monoacrylate is treated as a monomer of relative length $v_1=1$.

The order of magnitude of the diffusion coefficient is correct, as can be verified by Stokes law: $D=kT/(6\pi\eta r)$. Assuming a viscosity η of about $1\cdot 10^{-3}$ Pa·s [$\eta(\text{water})$]

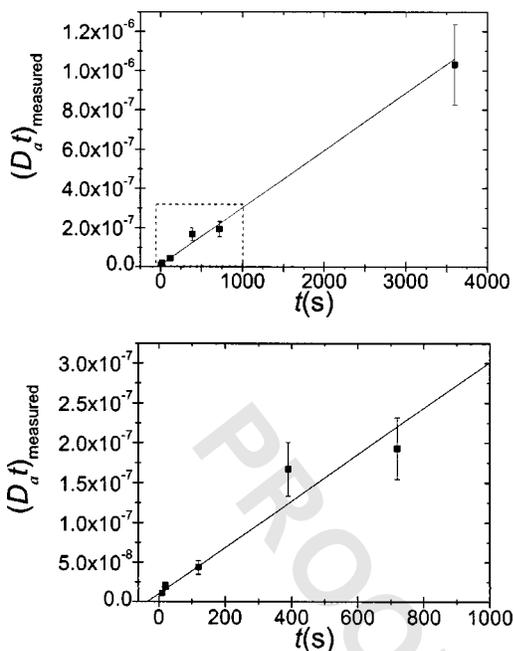


FIG. 5. The measured value of $D_a t$ vs the time t (top) and an enlargement of the boxed region (bottom).

$= 1 \cdot 10^{-3} \text{ Pa}\cdot\text{s}$, $\eta(\text{MMA}) = 0.56 \cdot 10^{-3} \text{ Pa}\cdot\text{s}$, $\eta(\text{hexanediol-dimethacrylate}) = 8 \cdot 10^{-3} \text{ Pa}\cdot\text{s}$], and a Stokes radius r in the order of 1 nm, it follows that $D \approx 2 \cdot 10^{-10} \text{ m}^2/\text{s}$.

It is assumed that the Flory–Huggins interaction parameters χ are zero. For the grating preparations,^{5,6} where one starts with a homogeneous mixture of two monomers, this is justified because the monomer units in both polymer and monomer are the same and that the differences in volume fraction between dark and illuminated regions are only about 10%. In the current article, however, the interaction parameters might play a more significant role since a whole range of volume fractions between $\varphi_1 = 0$ and $\varphi_1 = 1$ are involved, which means that some deviation between the measured and simulated diffusion profiles may occur.

CONCLUSIONS

It is shown that monomer diffusion profiles can very well be studied with a scanning proton microprobe if these

monomers contain elements that are easily detectable by PIXE, e.g., Cl and Si. From the diffusion profiles of the Cl-monoacrylate and the Si-dimethacrylate, it is possible to determine the mutual diffusion coefficient assuming a linear dependence of the mutual diffusion coefficient on composition: $D_a = (2.9 \pm 0.6) \cdot 10^{-10} \text{ m}^2/\text{s}$ at $\varphi_1 = \varphi_2 = 0.5$.

Since the Cl- and Si-profiles are asymmetric, the mutual diffusion coefficient depends on the volume fractions of the individual components. A linear dependence of the diffusion coefficient on the volume fractions has been used as a first-order approximation. The best fits of the diffusion profiles are obtained for a value of $b = 0.38 \pm 0.15$, which is the ratio of the diffusion coefficient of the Si-dimethacrylate in pure Cl-monoacrylate and the diffusion coefficient of the Cl-monoacrylate in pure Si-dimethacrylate.

Further, assuming a Flory–Huggins treatment of the chemical potentials and diffusion coefficients proportional to the molecule length, the intrinsic monomer diffusion coefficients can be determined.

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