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Measurements of polymer diffusion over small distances. A check of reptation arguments

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Abstract. — We performed neutron reflectometry (NR) and nuclear reaction analysis (NRA) measurements on interdiffusion of protonated and deuterated polystyrene films Covering several orders of magnitude in time t and resolving interfacial widths $w(t)$ between approximately 2 nm and 60 nm we found two successive time regimes with a crossover corresponding to the reptation time τ_d Below τ_d we are able to approximate the interface profile quite well by two superposed error functions described by three parameters, $\sigma_c(t)$, $\sigma_t(t)$ and $p(t)$ The two contributions are interpreted according to the Rouse and the reptation model While the width σ_c of the error function correlated to Rouse type motion stays almost constant, the width σ_t of the second contribution increases with time $p(t)$ represents the percentage of the second contribution at the interface It increases with time reaching 100 per cent at τ_d An explanation is given in terms of the reptation model The time behavior of $\sigma_c(t)$, $\sigma_t(t)$, $p(t)$ and $w(t)$ is discussed τ_d and $w(\tau_d)$ are determined independently using three different methods. All results are in qualitative agreement with the reptation model

Introduction.

The chainlike structure of polymers necessitates special mechanisms for the diffusion of these molecules. In a polymer melt the molecules are entangled, provided that they are long enough, and this has great influence on their mobility. Assuming the entanglement points to be fixed on the time scale of polymer movement over distances comparable to their size, the diffusion path is determined by these points. The molecules have to move along their contour in a tube [1] Within the tube polymer motion is also restricted because the chain segments are connected to each other like beads connected by springs (Rouse model [2]) Both constraints — the movement in the tube (this is usually called reptation) and the need of a correlated motion of the segments — result in a characteristic time behavior of polymer diffusion over distances shorter than the average size of the molecules [3].

Diffusion over distances less than the distance between entanglement points is governed by a Rouse type motion The limiting time for this process is τ_e. At this time the displacement of segments becomes comparable to the diameter of the tube At later diffusion stages the polymers are forced to move along their contour within the tube. As long as segmental motion is not correlated over the whole chain, i.e below a characteristic time τ_r (longest Rouse relaxation time), the displacement of molecules is restricted by two constraints. First, a segment has to take into account the movement of neighboring segments and second, its motion has to be within the tube This leads to a time exponent for the average displacement of segments of 1/8 compared to 1/2 and 1/4 for Fickian diffusion and Rouse type diffusion below τ_e, respectively. For times longer than τ_r but shorter than the reptation time τ_d, i.e the time a molecule needs to disengage from the original tube, the diffusion path of a molecule is still determined partly by the tube in which it was confined initially. This topological constraint leads to a $t^{1/4}$ behavior for this time regime. After times longer than τ_d a molecule has completely moved out of its original tube and its diffusion path can be chosen arbitrarily The time exponent of 1/2 occurs again as for Fickian diffusion

In order to investigate polymer diffusion in the time regimes discussed above, one can look at the intermixing of two polymer films which are brought in contact and are annealed above the glass transition temperature T_g Initially there are no molecules crossing the interface between the two films In order to interdiffuse the molecules have to move across the interface. However, according to the reptation model only those molecules can cross which have an end at the interface [4]. As a consequence there is a discontinuity in the concentration profile at the position of the interface for $t < \tau_d$, which is decreasing with time. The experimental evidence of such a discontinuity is an indication for hindered diffusion As such a discontinuity is predicted by the reptation model, its detection will confirm this model

The broadening of the interface can be measured by X-ray or neutron reflectrometry with a subnanometer resolution in depth for interfacial widths between 0 and 10-20 nm [5] One can also apply backscattering techniques [6, 7] as well as secondary ion mass spectrometry [8] with a resolution of several nanometers

In this paper we present neutron reflectrometry (NR) and ^{2}H(^{3}He, ^{4}He)^{1}H nuclear reaction analysis (NRA) measurements on the intermixing of deuterated and protonated polystyrene (PS) films. These techniques are complementary in two ways. As the reflectivity of a smeared interface is lower than that of a sharp one the resolution of NR is drastically worse for interfacial widths above 10-20 nm. NRA, on the contrary, cannot resolve interfacial broadening below approximately 10 nm mostly due to energy straggling.

NRA determines the interfacial concentration profile directly NR on the other hand yields reflected intensity as a function of angle and a model is needed to interpret these data in terms of a composition profile. NRA results can therefore be used to verify the models used for NR data analysis Applying these two techniques simultaneously on the same system one can profit of the advantages of each and therefore reduce possible ambiguities of either method

Experimental.

For our investigations we used protonated and deuterated polystyrene of high molecular weight M_w, 660 000 g/mol with $M_w/M_n = 1.1$ and 752 000 g/mol with $M_w/M_n = 1\ 2$, respectively, as determined by GPC. Thin films (60-80 nm for NR experiments and 200-300 nm for NRA measurements) were prepared by the spin coating technique. For NR we used float glass substrates of $100 \times 100 \times 3\ \text{mm}^3$ and for NRA silicon substrates of $20 \times 10 \times 0\ 25\ \text{mm}^3$ Double layer samples were prepared by floating the top film onto a water surface and picking it up with the bottom film which was directly spuncast onto the substrate After drying these samples below T_g for 12 to 24 hours they were annealed above T_g allowing interdiffusion of the polymers.

The NRA samples were sealed in glass tubes under vacuum ($\sim 10^{-5}$ mbar) and were annealed at $T = 140 \pm 0\ 5$ °C for from 5 hours up to 8 days The NR samples were annealed in a vacuum oven ($\sim 10^{-1}$ mbar) at different temperatures (122-134 °C, except for the first point where the sample was annealed for 30 min at 112 °C) between 50 min and 10 hours

To cover several orders of magnitude in time, we had to vary the annealing temperature and account for the higher mobility of the polymers by a shift factor a_T given by the WLF equation This equation has been verified experimentally for our system by Tassin and Monnerie performing mechanical measurements [9] a_T is given by the following expression for a reference temperature of 120 °C

$$\log a_T = \frac{-9.06(T-120)}{69.8+(T-120)} \tag{1}$$

The actual annealing times are divided by a_T in order to get annealing times reduced to the reference temperature of 120 °C It is not quite clear if equation (1) holds for small diffusion paths One might assume that different processes are involved at short length scales. We have measured several samples at different temperatures and did not notice any indication for this assumption. In the region of the crossover of the two techniques, the annealing temperatures differ only by about 10 degrees. Thus in this region the errors introduced by the use of equation (1) are supposed to be small

Neutron Reflectometry (NR)

The single films as well as the double layer samples have been characterized by X-ray reflectrometry [10]. From these measurements we know the thicknesses of the layers and the roughness at the surface and at the substrate of our samples These pieces of information are used for the analysis of the neutron reflection data which were measured on TOREMA [11] at the KFA Jülich. A typical run took about 12 hours and reflectivities below 10^{-4} were reached TOREMA operates with a monochromatic beam at a fixed wavelength of 0 43 nm. Therefore at this machine we have to rotate the sample and measure the reflected intensity as a function of the angle of incidence. The technique is explained in more detail elsewhere [12].

Assuming Gaussian distributed roughness for the interfaces and close contact between the layers the refractive index profiles at the interfaces can be described by error functions with a characteristic parameter σ [13] Such a profile implies that the sample has the same roughness over the whole area illuminated by the neutron beam as well as equal chemical composition and density at the surface and in the bulk However, there are possibilities where this is not justified. For example, oxide layers on silicon, higher water concentration on the glass surface compared to the bulk, or a layer of water between the polymer films or between the polymers and the substrate lead to deviations from an error function profile In our experiments we had to consider deviations of this type for the interface at the glass substrate. We used a refractive index profile which has a rather steep change from the polymer layer to the glass but then reaches only slowly the bulk value of glass This profile does not change during the different stages of annealing and even can be fixed for the evaluation without a significant influence on the parameters of the polymer-polymer interface If we use a simple error function profile we get considerable deviations between measured and simulated data especially in the region close to the critical angle for total reflection. These deviations occur at the same region of the angle of incidence and are equally large for all stages of annealing Moreover, we found the same type of profile as used for the analysis of the present data for all glass substrates we have used for neutron reflection measurements up to now More details will be reported in a subsequent publication [14].

As we are examining interdiffusion of two polymer films we have to determine the interface profile between these films as accurately as possible. We are not able to describe this interface appropriately by a single error function profile. In particular the data of the annealed sample showed that we can fit the data at large angles quite well with a rather small value of σ, however large differences appear at small angles. On the other hand we can fit the data at small angles by using a larger value of σ but then it is impossible to fit the data at large angles. This observation led us to use a superposition of two error functions according to the following equation for the refractive index (which is proportional to the polymer concentration) as a function of depth z:

$$\begin{aligned} n(z) &= \Delta n\left\{(1-p)(2-\operatorname{erfc}(z/\sigma_{\mathrm{c}}))+p(2-\operatorname{erfc}(z/\sigma_{\mathrm{t}}))\right\} \\ \operatorname{erfc}(z) &= 1-\operatorname{erf}(z) \end{aligned} \tag{2}$$

where Δn is the difference in refractive index between deuterated and protonated polystyrene The core region around the midpoint of the resulting profile is mainly described by σ_{c} whereas σ_t accounts for the tails of the profile ($\sigma_{\mathrm{c}} < \sigma_t$) The parameter p determines the percentage of the contribution of the second error function to the profile The shape of this profile thus depends on three parameters, σ_{c}, σ_t and p. The same type of profile for the polymer-polymer interface was found for all measured samples.

The fitting was done by a semiautomatic program on the basis of a matrix formalism [15] with all parameters being variable The difference between the experimental points and the simulated values weighted by the experimental error was minimized The increment by which the parameters can be varied by the program is fixed.

In figure 1 we show three measured reflectivity curves together with the best fits. The deviations are small, which shows that our model is appropriate to describe our data For the different stages of annealing only the three parameters of the interface between the two polymer layers change significantly. All other parameters are constant within their error although we allowed these parameters to be varied during the fit Moreover, we obtain equally good fits, if we take all parameters except the three parameters of the polymer-polymer interface fixed to the same values for all stages of annealing.

Typical results of the NRA measurements are shown in figure 2

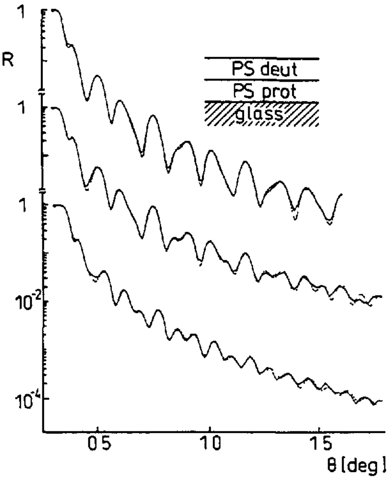

Fig 1 — Measured neutron reflectivity R *versus* incident angle θ (full lines) for three stages of annealing for a bilayer system of deuterated and protonated polystyrene on a glass substrate Beginning from top we show the results for the unannealed, 2 min and 3 900 min annealed sample used in this work The annealing temperatures are reduced to a reference temperature of 120 °C The data are compared to the best fits (broken lines) according to a model described in text The model profile of the interface between the polymer layers can be seen in figure 3 and figure 4

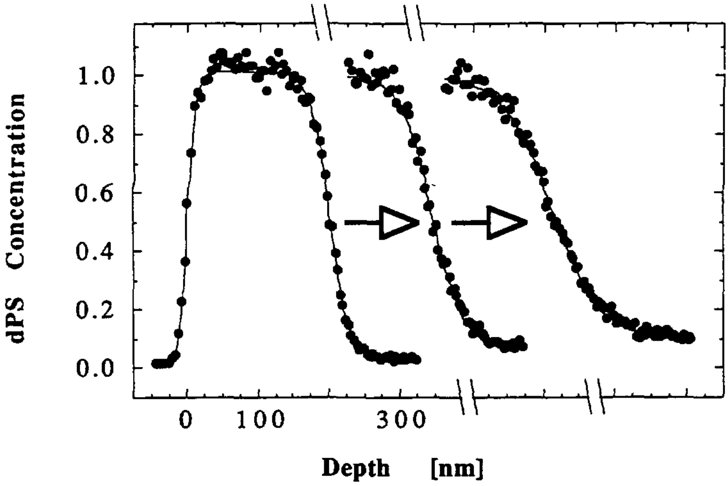

Fig. 2 — Deuterium concentration *versus* depth measured by nuclear reaction analysis for a bilayer system of deuterated and protonated polystyrene on a silicon substrate Three different stages of annealing are shown From the left to the right unannealed, 140 °C for 3 430 min and 140 °C for 10 280 min

Figure 3 shows the profiles we obtained from the best fit for the unannealed and the annealed stages The inset of this figure shows the long range contribution of the profile (see Fig. caption) The two contributions to the profile and the summed profile for different stages of interdiffusion are shown in figure 4 The core region of the profile remains almost unchanged for all measurements except a significant increase after the first annealing The

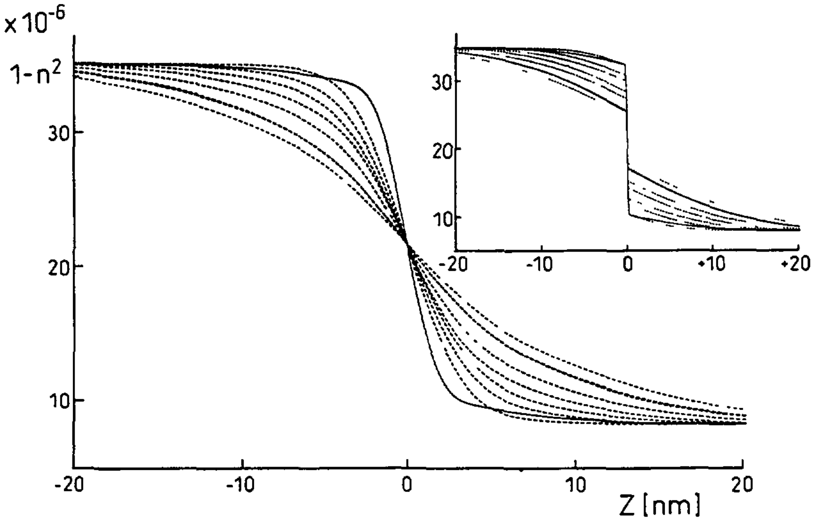

Fig 3. — Refractive index profiles of the interface between the polymer layers used for the evaluation of the neutron reflectivity data The position of the interface is given by $z = 0$ On the ordinate we plot $1 - n^2$, where n is the refractive index The inset shows the contribution of σ_t and p according to the following equation : $n(z) = p \, . \, \Delta n \, [2 - \text{erfc} \, (z/\sigma_t)] + (1 - p) \, . \, \delta \, (\Delta n)$ with $\delta(\Delta n) = 0$ for $z < 0$ and Δn for $z > 0$ Explanations of the different parameters are given in text The full lines represent the data for the unannealed sample The different stages of annealing are shown by the broken lines

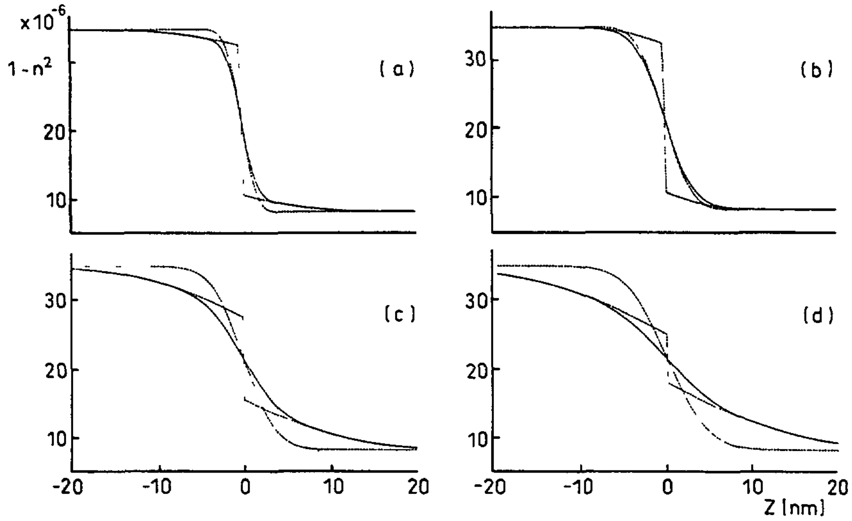

Fig 4 — Refractive index profiles of the interface between the polymer layers used for the evaluation of the neutron reflectivity data (full lines) For comparison the different contributions to the profile according to the model are indicated by the broken lines Four different stages of annealing are shown (a) unannealed, (b) 2 min annealed, (c) 3 900 min annealed and (d) 25 000 min annealed The annealing times are reduced to a reference temperature of 120 °C by the use of the WLF equation [9]. The continuous part ($n(z) = \Delta n \,.\, \mathrm{erf}\ (z/\sigma_c)$) is interpreted by Rouse type motion within the tube and stays constant The second part [$n(z) = p \,.\, \Delta n\,[2 - \mathrm{erfc}\ (z/\sigma_t)] + (1 - p) \,.\, \delta\,(\Delta n)$ with $\delta\,(\Delta n) = 0$ for $z < 0$ and Δn for $z > 0$] with a discontinuity at $z = 0$ corresponds to reptation of molecules over distances larger than the tube diameter

tails of the profile get more and more dominant with increasing annealing time. Both σ_t and p are increasing The variations with time of σ_c, σ_t and p are shown in figure 5 The plotted values are corrected for the initial roughness contribution $x^2_{\text{corrected}} = x^2_{\text{measured}} - x^2_{\text{initial}}$ with x equal σ_c, σ_t or p

We determined the interfacial width $w(t)$ by calculating the standard deviation (SD) for the polymer polymer interface profile according to

$$\mathrm{SD} = [(1 - p)\,\sigma_c^2 + p\sigma_t^2]^{1/2} \tag{3}$$

and corrected it for the initial value due to roughness

$$\begin{aligned} w(t) &= \mathrm{SD}_{\text{corrected}} \\ &= (\mathrm{SD}^2_{\text{measured}} - \mathrm{SD}^2_{\text{initial}})^{1/2} \end{aligned} \tag{4}$$

The values of $w(t)$ are shown in figure 6 together with the uncorrected values of the unannealed and only once annealed sample. There is no significant difference in $w(t)$ between the two uncorrected points although σ_c increases from 1.3 to 2.4 nm Because of the quadratic averaging the σ_t contribution dominates. Therefore a small interfacial broadening due to roughness on the length scale of σ_t (possibly caused by defects due to preparation like small folds or others produced during the floating of the top film) can determine $w(t)$ This gives the lower limit for the interfacial width due to diffusion we can measure The broadening of the interface caused by diffusion has to be larger than the smearing of the profile due to roughness in order to be seen

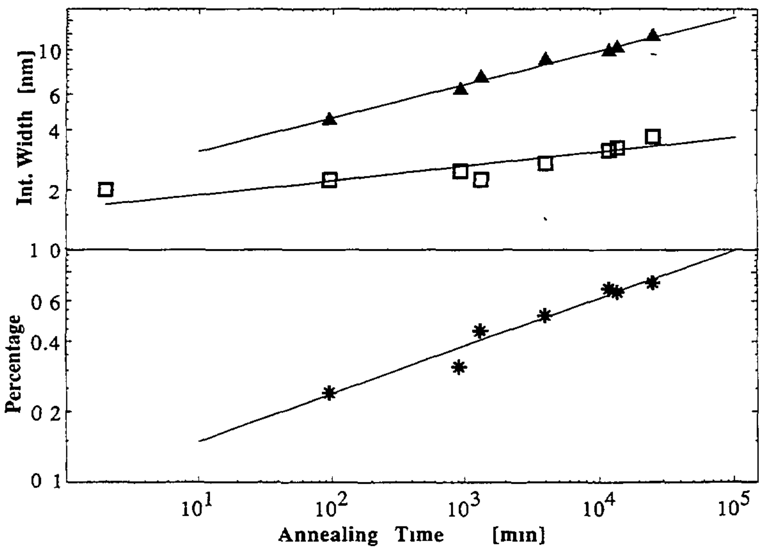

Fig 5 — Double logarithmic plot of the model parameters p (stars), σ_c (squares) and σ_t (full triangles) *versus* time (reduced to the reference temperature of 120 °C) Initial roughness is subtracted according to equations given in the text The best fit according to $x \sim t^{\nu}$, x being p, σ_c or σ_t, yields 0.22, 0.07 and 0.17, respectively

Nuclear reaction analysis (NRA)

The development of interface formation for interfacial widths larger than 10 nm was monitored by the ^{2}H(^{3}He, ^{4}He)^{1}H nuclear reaction analysis (NRA). The details of this technique are described elsewhere [6]. A 900 keV ^{3}He beam impinges on the polymer film and undergoes a nuclear reaction with the ^{2}H atoms of the deuterated polymer species The resulting ^{4}He particles are detected by an energy dispersive detector under a forward angle of 30° A magnetic filter is employed to separate the ~ 6 MeV ^{4}He particles from the low energetic elastically scattered ones.

The resulting energy spectrum contains information on the distribution of deuterium atoms (^{2}H) in the sample. After correction for cross-section and normalization the analysis of the energy spectrum in terms of nuclear stopping powers yields the depth-concentration profile of the deuterated polymer species (Fig. 2) When measuring concentration profiles of deuterated polystyrene, we are able to achieve a spatial resolution of ca 14 nm full-width-half-maximum (FWHM) at the sample surface and ca. 25 nm FWHM at a 200 nm depth [6]

A convenient measure to define the interfacial width of the NRA diffusion profile is the interquartile width, defined by the distance $d_{\mathrm{exp}} = z(\phi = 0.75) - z(\phi = 0.25)$, where ϕ is the concentration of deuterated molecules d_{exp} is corrected for the instrumental broadening d_0 by quadratic subtraction : $d(t) = [d_{\mathrm{exp}}(t)^2 - d_0^2]^{1/2}$. To compare the results determined by NRA with the profiles obtained by neutron reflectrometry, we relate the interquartile width d to the standard deviation of an error-function SD by $\mathrm{SD} = \beta \, . \, d = w(t)$, where $\beta = 0.74$. β is calculated by determining the interquartile width of an error function $\sigma = 1$; $1/\beta = z(\mathrm{erf}\ (z) = 75\ \%) - z(\mathrm{erf}\ (z) = 25\ \%)$.

Results and discussion.

The development of the interfacial width $w(t)$ with time is shown on a double logarithmic plot in figure 6. The variation of $w(t)$ with time is well represented by two power law relations $w(t) \sim t^{\nu}$. A linear regression of the NRA data (represented by full diamonds in Fig. 6) with respect to log $(w(t))$ and log (t) yields the exponent to $\nu = 0.53 \pm 0.03$. This compares to the power variation which describes free, unrestricted interdiffusion where the exponent is predicted to be $\nu = 1/2$.

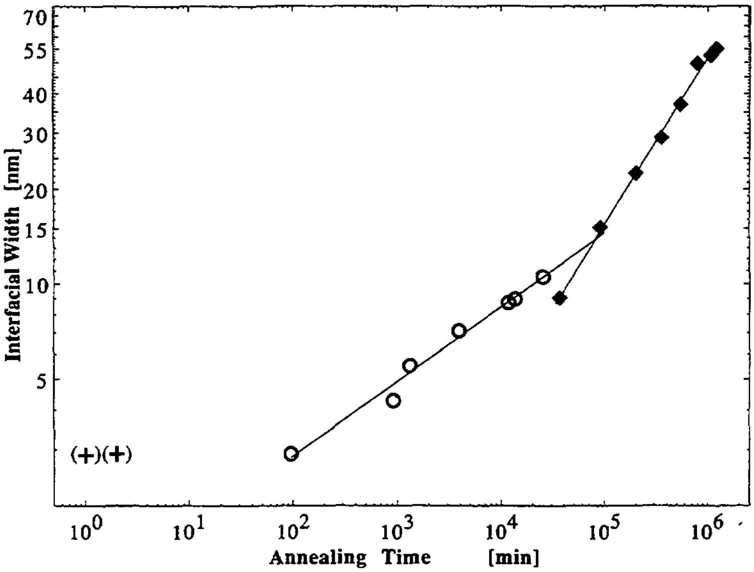

Fig. 6 — Double logarithmic plot of the interfacial width $w(t)$ *versus* time (reduced to the reference temperature of 120 °C) for NRA data (full diamonds) and NR data (circles). The data are corrected for initial roughness according to the equations given in the text. The two crosses in brackets represent the results for the unannealed (time arbitrarily set $t = 1$ min) and the once annealed sample ($t = 2$ min) without correction. These two points determine the lower limit of $w(t)$ which could be measured.

Assuming $\nu = 1/2$, we are able to determine the diffusion coefficient for our system $D = w^2(t)/2\,t$. A linear regression of $w^2(t)$ *versus* t yields the diffusion coefficient: $D = (2.44 \pm 0.13) \times 10^{-17}\ \mathrm{cm^2/s}$ (for $T = 140$ °C). A comparison to other studies has to take into account thermodynamic slowing down [16] due to a non-zero interaction parameter χ between deuterated and protonated molecules

$$D = \Omega(\phi) \cdot [\chi_s(\phi) - \chi] \tag{5}$$

$$\Omega(\phi) = 2\,\phi\,(1 - \phi) \cdot [D_d^*\,N_d(1 - \phi) + D_p^*\,N_p\,\phi] \tag{6}$$

$$\chi_s(\phi) = [(N_d\,\phi)^{-1} + (N_p(1 - \phi))^{-1}]/2 \tag{7}$$

with ϕ being the volume fraction of deuterated molecules, N_d and N_p the number of monomers, D_d^* and D_p^* the tracer diffusion coefficients of the deuterated and the protonated molecules, respectively.

Doing the calculation according to equations (5)-(7), using tracer diffusion coefficients as determined in reference [17], extrapolated to the molecular weights and annealing temperature used in our investigations, and a molecular interaction parameter χ from reference [18], we calculate the diffusion coefficient to be 2.64×10^{-17} cm^2/s Considering the large error in the calculation, due to the extrapolation procedure and to the large error in the molecular interaction parameter, we find extremely good agreement of the diffusion coefficient measured here with the calculated value.

Even though diffusion in this time regime (i e. for diffusion paths larger than the spatial extent of the polymer molecules) is described by Fickian diffusion and mechanisms that occur at spatial scales of a single polymer coil do not play a role, information about these mechanisms can be obtained from NRA data. One can compute the crossover point from reptation to unrestricted diffusion according to references [1, 3] A change in the time dependence of diffusion is predicted at $\tau_d = (Nb^2)/(3\,\pi^2 D_{cm})$ with b the statistical length of a segment and D_{cm} the center of mass diffusion coefficient Taking the value of $b = 0\,67$ nm from literature [18] and for D_{cm} the value we have measured (reduced to 120 °C by using Eq. (1) [19]) we can calculate τ_d to be 6.85×10^4 min. The interfacial width at this time is 12.7 nm (determined from the NRA data of Fig. 6) which is comparable to the value we would expect for polymer diffusion across an interface [$w(\tau_d) = \frac{1}{\sqrt{3}} \cdot \frac{\sqrt{2}}{\pi} \cdot R_{ee} =$ 14 nm with $R_{ee} = (Nb^2)^{1/2}$ being the end-to-end distance of the molecules [3, 20]].

Summarizing the results of the NRA measurements we found an exponent of approximately 1/2 for the time dependence of the interfacial width, a diffusion coefficient in agreement with previous measurements and we have been able to determine τ_d and $w(\tau_d)$. Due to the check with results reported in literature the value of τ_d is highly reliable. Thus a criterion for the quality of the NR results is the correspondence of the value of τ_d extracted from the NR data with the value obtained from the NRA measurements. The application of NRA allows us to get an indication, if the model used for the analysis of the NR data is correct.

The analysis of the NR data revealed that the interface profiles between the polymer films cannot be described by a single error function. They are better approximated by the use of two superposed error functions. An interpretation of the three parameters of the two functions can be given in the following way Assuming that polymer diffusion is determined by the movement along the tube the molecules can leave the tube by their ends only. Consequently at $t = 0$ only ends of molecules which are at the interface can cross the interface. After one reptation time τ_d all molecules have been able to cross the interface at least by an end. This causes a discontinuity of the profile at the position of the interface for times shorter than τ_d. On the other hand, the mobility within the tube is not restricted and thus the discontinuity is smeared out. Whereas all segments at the interface have the possibility to move over distances smaller than the tube diameter, the probability P for diffusion over larger distances is $P = 2/N$ at $t = 0$ (assuming uniform distribution of ends) and $P = 1$ at $t = \tau_d$. This can be described by a superposition of two profiles a continuous one with a maximum width comparable to the tube diameter and a discontinuous one with a width determined by the average distance the molecules have moved away from the interface. As the number of segments which are able to cross the interface via reptation increases with time the discontinuity decreases If we assume that the parameter p used for the analysis of the NR data describes the probability P we determine τ_d by extrapolating p to $p = 1$ for the best fit of $p \sim t^{\nu}$ to the data plotted in figure 5, resulting in $(t(p = 1)) = 1.04 \times 10^5$ min for the reference temperature of 120 °C The average distance the molecules have moved by this time is then given by the extrapolation of $\sigma_t \sim t^{\nu}$ for $t = t(p = 1)$ The result is $\sigma_t(t(p = 1)) = 14\,5$ nm Thus, τ_d and $w(\tau_d)$ have been determined in a second independent fashion. The two results compare quite well

The third possibility to determine τ_d and $w(\tau_d)$ is given by the crossover between the regime of Fickian diffusion ($w \sim t^{1/2}$) and the reptation regime, as discussed in the introduction We observe this crossover by combining NR and NRA data as shown in figure 6 with $\tau_d = 8\ 2 \times 10^4$ min and $w(\tau_d) = 13.9$ nm Although we do not have an overlap region between both techniques due to experimental limitations the crossover point can be determined accurately by extrapolation of NR and NRA data The values of τ_d and $w(\tau_d)$ as obtained by three independent procedures are in reasonable agreement. Again, this correspondence indicates the validity of the three methods we used to determine τ_d and $w(\tau_d)$.

So far everything fits to the predictions of the reptation model However the exponents of the time behavior $x \sim t^{\nu}$ where x represents σ_c, σ_t, p and $w(t)$ are more difficult to interpret. Our measurements yield 0 07, 0 17, 0.22 and 0.24, respectively. Assuming that σ_c describes Rouse type mobility within the tube it seems quite obvious that σ_c should be constant up to τ_d. If we take σ_c fixed for the evaluation of the NR data we get the following exponents for σ_c, σ_t, p and $w(t)$: 0 00, 0 14, 0 24 and 0.22, respectively.

The decrease of the discontinuity and the increase of the number of molecules crossing an interface has been treated theoretically by several authors [21, 22, 4] They get a time dependence of $P \sim t^{1/2}$ This in contradiction to $t^{0\ 22}$ An estimation of possible errors shows that the discrepancy is too large and cannot be explained by experimental uncertainties, as we show in the following paragraphs.

The largest errors originate from a non precise subtraction of the roughness contribution. The actual roughness is basically unknown because of interface healing effects during annealing at short times Therefore it cannot be determined reliably by measuring the unannealed sample From measurements of comparable samples annealed at approximately T_g we know that changes of the interface are small (smaller than the effects seen for the first annealing shown in Fig 3 and Fig 4) but unpredictable because they depend strongly on sample preparation and are different for each sample

A second source of errors arises from an inadequate model for the interface profile Deviations between the actual profile and our model profile originate mainly from the description of the tail contribution by a simple error function profile σ_t is not accurately representing the root mean square displacement of the molecules across the interface according to the reptation model The function describing the distribution of segments has to take into account the increasing number of molecules which can cross the interface with increasing time Also the effect of Rouse type motion within the tube and simultaneous reptation of the molecules has to be considered at any distance from the interface. However, near the interface Rouse type motion dominates and at large distances reptation determines the profile Therefore we assume that the superposition of the effects of both types of motion corresponding to equation (2) is approximating the profile reasonably well Nevertheless it would be better described mathematically by a convolution of three effects : Reptation and simultaneous Rouse type mobility as well as the hindrance of reptation across the interface if the molecule has no end at this interface. At present no analytical solution for such a profile is available [23].

The errors of $\sigma_t(t)$ and $p(t)$ also influence the values of $w(t)$ calculated according to equation (3) and thus also the time behavior of $w(t)$

Taking all these systematic uncertainties into account, we have to allow fairly large error margins for the experimentally determined time exponents However, these errors do not account for the difference (approximately a factor of two) between the experimentally observed values and the ones predicted by theory

A possible explanation of the exponents deduced from our experiments would be the attraction of ends to the surface [24]. Assuming that all molecules which have a segment at the surface also have an end there, the expected time dependence of the parameter p would be $p \sim t^{1/4}$ However, there are also other arguments which have to be considered. The preparation technique as well as the small thickness of the films might induce non equilibrium conformations which might affect the time dependence of polymer interdiffusion. Rouse type mobility might also allow for a higher number of molecules to cross the interface almost from the beginning. Finally, one might ask if the mobility of parts of the molecules is the same as for the center of mass For example it is shown by computer simulations that the ends of the molecules are more mobile than the center [25] Nevertheless the experimental determination of exponents is an ambitious task because systematic errors arising from background subtraction or our model assumptions affect the resulting values to a large extent. Better sample preparation, still more accurate reflectometry measurements and a more complex description of the interface profile are required to determine these exponents more accurately and to be able to give an explanation of them

Conclusions.

We performed nuclear reaction analysis (NRA) and neutron reflectometry (NR) measurements on the interdiffusion of deuterated and protonated polystyrene films. NRA determines the interfacial profile in a direct way whereas a model is needed for the evaluation of the NR data. Both methods are complementary with respect to their depth resolution They supplement each other and their combination avoids uncertainties arising from the use of a single technique.

The analysis of the NRA data shows that the interfacial width $w(t)$ grows according to Fickian diffusion with $t^{1/2}$. We determine the center of mass diffusion coefficient D for our system for a temperature of 140 °C : $D = 2\ 44 \times 10^{-17}\ \mathrm{cm^2/s}$ Knowing D we calculate the reptation time τ_d and $w(\tau_d)$

The evaluation of the NR data yields a complex profile (σ_c, σ_t, p) which can be interpreted as the superposition of displacements of molecules according to Rouse type motion and reptation The contribution due to reptation (σ_t, p) is increasing with time whereas the part (σ_c) due to Rouse type mobility stays nearly constant with time. The reptation contribution is discontinuous at the position of the interface for $t < \tau_d$ as predicted [4] Extrapolation of the decrease of this discontinuity with time (increase of p) to the time where it vanishes yields τ_d and $w(\tau_d)$ At τ_d all molecules which had a monomer at the interface at $t = 0$ have been able to cross

The third way to determine τ_d and $w(\tau_d)$ is given by the crossover from restricted diffusion due to the tube constraint to unhindered Fickian diffusion.

We get the following results for τ_d and $w(\tau_d)$ From the diffusion coefficient extracted from the NRA data we compute $\tau_d = 6.85 \times 10^4$ min and $w(\tau_d) = 12.7$ nm, from the NR data and the vanishing of the discontinuity we derive $\tau_d = 1\ 04 \times 10^5$ min and $w(\tau_d) = 14.5$ nm and finally, the crossover of the time behavior of $w(t)$ yields $\tau_d = 8.2 \times 10^4$ min and $w(\tau_d) = 13.9$ nm All values, determined independently by three different methods, agree well within the experimental error.

The evidence for a discontinuity of the interfacial profile which vanishes with time, the constant core contribution due to Rouse type mobility and the 3-fold coincidence of τ_d and $w(\tau_d)$ agree qualitatively with predictions of the reptation model [1, 4]. However, the exponents found for the time behavior of σ_t, p and $w(t)$ do not correspond to the values expected by theory assuming uniformly distributed ends of the molecules To resolve this issue further measurements have to be performed.

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