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Diffusion of linear polystyrene into crosslinked polystyrene

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The diffusion of linear polystyrene (PS) into its crosslinked counterpart was studied using both neutron reflectivity (NR) and forward recoil scattering (FRES). The penetrant molecular weights were monodisperse and ranged from 10 000 to 690 000 g mol^{-1}. The molecular weight between crosslinks was kept at 22 000 g mol^{-1}. The crosslinks were introduced by polymerizing styrene monomer in the presence of divinylbenzene. The FRES results revealed the presence of a high molecular weight cut-off for the linear PS above which diffusion could not proceed. The NR results indicated that even at these high molecular weights a certain amount of diffusion did occur but was confined to the first few hundred Angstroms of the interface. A step function in the polymer concentration profile was found at these high molecular weights as expected for systems showing a limited solubility for the diffusant. The counter diffusion of residual sol from the crosslinked network is used to explain certain features of the diffusion profile. © 1997 Elsevier Science Ltd.

(Keywords: diffusion; crosslinked network; concentration profile)

INTRODUCTION

The diffusion of linear polymer chains into crosslinked polymer networks is a topic of practical importance about which there is little fundamental understanding. From the repairing and bonding of thermoset composite parts, to the creation of polymer laminates, the diffusion of linear chains into crosslinked networks plays a prominent role in the manufacture and application of polymeric materials. Nevertheless, there remains a long-standing question as to the basic shape of the concentration profile at an interface between a material consisting of linear polymer chains and one comprised of a crosslinked polymer network. The microscopic shape of this concentration profile is inextricably linked to the macroscopic performance of the interface, e.g. its peel strength. Understanding the shape of this profile will, in turn, lead to better control of its macroscopic properties.

Prior experiments have been conducted on the closely related question of the compatibility and conformation of linear chains embedded in crosslinked networks. Typically, samples were made by introducing crosslinks into a mixture of linear chains and a crosslinkable species[1,2]. Under these circumstances, the networks were formed concomitantly with the redistribution or expelling of the linear species. Since this is a complex process, an open question remains as to the state of equilibrium in the resulting network. For network formation in the presence of a low molecular weight solvent, the redistribution of the solvent can be rapid and the network can reach its equilibrium condition. For the case of high molecular weight chains as the diluent, the redistribution rate depends on the diffusion coefficient between the linear diluent and the partially-formed network. This coefficient may be rather low and the resulting network may not be formed at equilibrium conditions, or even at conditions which can be fully characterized and reproduced. To avoid this circumstance, the present study uses a well-defined network that was fully formed before the diffusing species was brought into contact.

Diffusion of linear chains into networks has also been a topic of prior study[3–8]. Most of the previous work focused on the condition where the molecular weight between the crosslinks was greater than, or equal to, that of the linear chains. In the present work, the linear penetrant molecular weight ranged from below the molecular weight between the crosslinks to more than an order of magnitude above. Prior experimental studies used either forward recoil scattering (FRES)[3–5] or secondary ion mass spectroscopy (SIMS)[8] to determine the shape of the concentration profile. The depth resolution of these techniques is at best 50 Å but is generally much poorer. At the interface between a linear penetrant and a crosslinked network, one expects to observe a sharp drop in the composition profile falling from pure penetrant to some finite solubility limit. This is because, for polymeric networks, the swelling ratio must be finite since the chains connecting adjacent junctions

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*To whom correspondence should be addressed cannot be extended beyond their contour length. Such a sharp interface has yet to be reported. This may be due, in part, to a lack in the depth resolution of the techniques previously used.

In the present study, this sharp interface in the concentration profile has been observed. This observation rests on two important aspects of the experiment: first, the careful preparation of precured networks with a well-defined crosslink density and extremely flat surfaces and, second, the use of neutron reflectivity (NR) with its depth resolution of the order of ångstroms. Forward recoil scattering (FRES) is used to confirm the neutron reflectivity results but is rather insensitive to the sharp interface in the concentration profile due to its limited spatial resolution.

The objective of the present study is two-fold: to determine the penetrant concentration profile inside the network, and to determine the molecular weight dependence its diffusion rate, especially in the region where the diffusant molecular weight is greater than the network molecular weight.

EXPERIMENTAL

Sample preparation

The crosslinked hydrogenated polystyrene (HPS) blanks used were 50 mm in diameter and 2 mm thick. They were made from distilled styrene monomer with 0.5% wt benzoyl peroxide as the free radical initiator and 0.45% wt divinylbenzene as the crosslinking agent. The cure was conducted in dry nitrogen atmosphere and began at 70°C for 8 h followed by additional curing to 120°C for 12 h. The crosslink density of the resultant material was determined from its equilibrium swelling ratio in toluene. The Flory–Rehner equation was used for calculating the crosslink density with 0.44 used as the Flory–Huggins parameter between HPS and toluene. The resultant value for the molecular weight between crosslinks was 22 000 g mol^{-1}. One side of the mould used for making the crosslinked networks was a 75 mm diameter highly polished silicon single-crystal wafer. When removed from the mould, the resultant crosslinked network surface, which was in contact with the wafer during curing, was as smooth as that of the polished wafer. This smooth surface was the one used in all the diffusion studies.

The sol fraction of the cross linked materials was determined by solvent extraction. Crosslinked samples after NR measurements were allowed to swell in excess toluene for 2 days. After drying the weight loss was measured. The molecular weight of the extracted sol was determined by gel permeation chromatography and found to have a very broad molecular weight distribution with a significant fraction below 10 000 g mol^{-1}.

The samples for NR study were prepared as follows. Linear deuterated polystyrene (DPS) with molecular weights of 10 500, 27 000, 90 000, 401 000 and 690 000 g mol^{-1} (Polymer Laboratory*, Cambridge, MA) in 0.9% wt toluene solution were spin coated at 2000 rpm onto 50 mm diameter silicon wafers. (Deuteration is used to provide contrast in the NR and FRES measurements.) The value of M_w/M_n for each of the DPS molecular weights was around 1.05. The silicon wafers, with their native oxide layer intact, were cleaned in toluene followed by 3 min in an u.v./ozone cleaner to remove any residual traces of organic contamination. The DPS-coated wafers were dried in a vacuum oven at 120°C for 6 h to remove any remaining solvent. The film thicknesses were between 300 and 500 Å depending on the PS molecular weight with the higher molecular weights tending to result in thicker films. Within the NR measurement chamber, the flat surface of the crosslinked hydrogenated polystyrene (XHPS) blank was brought into contact with the DPS-coated silicon wafer.

For the FRES measurements the DPS films were first spin coated onto glass substrates. After being floated off the glass substrates and onto the surface of a distilled, deionized water bath, the DPS films were placed onto the smooth surface of XHPS blanks. For each FRES measurement a new sample was prepared. This is because the incident $^4H^+$ ions used in the analysis cause significant damage to the PS samples rendering them unsuitable for further annealing and measurement. This is in contrast to the neutron reflectivity measurements. After completing a given annealing sequence and NR measurement, the same sample was further annealed and measured again with NR. The neutron flux is not expected to inflict any significant damage to the sample, primarily because neutrons, being uncharged, have a very weak interaction with matter.

Different annealing temperatures were chosen for NR samples for the different molecular weights of the linear diffusant in order to keep the annealing time within the similar range. For samples with high molecular weight DPS, their diffusion rates were expected to be slow, thus high annealing temperatures were used to compensate for their slow rate. More specifically, at any given temperature, a polymer's diffusion constant is related to its molecular weight M through a M^{-2} dependence[9]. One can change the diffusion constant by varying temperature. The WLF relation was used for estimating this temperature dependence. We chose 690 000 g mol^{-1} DPS at 174°C as the reference point, for any other molecular weight, a temperature can be found where the diffusion constant is expected to be identical to that of 690 000 g mol^{-1} DPS. This temperature is called the equivalent annealing temperature. The WLF-type relation between diffusion constant and temperature can be written as:

$$\log\frac{D}{T} = A - \frac{B}{T - T_\infty} \qquad (1)$$

where T_∞ and B were chosen to be 322 and 710 K, respectively, which are typical values for polystyrene, and A is a constant whose value will not affect our discussion. T_∞ is related to the glass transition temperature T_g by $T_\infty = T_g - 50°C$. Glass transition temperatures change with polystyrene molecular weight through the following relation[10]:

$$T_g = 100 - \frac{1 \times 10^5}{M} \qquad (2)$$

For example, based on the two above equations, the equivalent annealing temperatures for 27 000 and

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*Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the items identified are necessarily the best available for the purpose

401 000 g mol^{-1} are 133 and 162°C, respectively. After annealing at these elevated temperatures for a predetermined time, samples were cooled at 90°C and NR data were collected.

Neutron reflectivity measurements

All the NR results were obtained from the POSY II reflectometer at the Intense Pulsed Neutron Source of Argonne National Laboratory. Data were collected at three different incident angles, 0.4, 0.9 and 1.5°, and were then merged to form a single reflectivity curve. The reflectivity was performed through the wafer such that the neutron beam approached the interface from the DPS side.

The ability of neutron reflectivity to probe buried interfaces results from the penetration power of neutrons through a variety of single crystals. In these experiments, silicon single crystal wafers with a diameter of 50 mm were used. With an attenuation factor of less than 8% for a beam path of 50 mm, the wafer is essentially transparent to the neutron beam.

The concentration profiles are reported in units of the elastic coherent-scattering length per unit volume, designated as Q_c^2. The name derives from the fact that Q_c^2 is proportional to the second power of the critical angle defined in terms of the magnitude of the momentum transfer normal to the interface: $Q_c = (4\pi/\lambda)\sin\theta_c$. Total reflection of neutrons with wavelength λ will occur if the incident angle is less than θ_c. It is important to note that in the above definition of Q_c or θ_c, the interface between the material and vacuum is considered. Q_c^2 can be regarded as the height of the neutron potential 'barrier' for the interface. If the energy of the neutron beam impinging on the surface is less than Q_c^2, total reflection occurs. More explicitly, $Q_c^2 = 16\pi Nb$ where N is the number density of scattering nuclei and b is their average scattering length. For silicon Q_c^2 is 1.06×10^{-4} Å^{-2}. Modelling and fitting of the neutron reflectivity data was by non-linear least squares fitting of profiles generated using a recursive multilayer method[11]. The amplitude of neutron reflection, in the Born approximation, is proportional to the first derivative of the neutron depth profile normal to the surface. Thus, abrupt changes in the depth profile result in certain prominent features in the NR results. Note that the depth profile probed by NR is a laterally averaged one over the cohesive length of micrometres. Lateral fluctuations can blunt a sharp transition to a gradual one. This point will be considered in detail in the Discussion section.

The XHPS blank and the DPS film were brought into contact and then placed inside the NR chamber which was subsequently evacuated to a pressure on the order of 10^{-2} Pa (10^{-4} Torr). A metal spring behind the XHPS blank kept the assembly under constant load throughout the measurement. The samples were annealed at a given temperature for a certain time and cooled to 90°C at which temperature all the NR measurements were made. Lowering the temperature to below 90°C resulted in a build up of interfacial stress between the silicon wafer and the XHPS blank owing to the large difference in their thermal expansion coefficients. This often led to debonding along the DPS/Si interfaces. NR results from debonded samples, especially partially debonded ones, are difficult to interpret and are not considered in this work.

Forward recoil scattering measurements

Forward recoil scattering (FRES) measurements were conducted at the University of Pennsylvania Ion Scattering Central Facility with 2 MeV $^4He^+$ ions incident on the sample at 75° from the surface normal. The total scattering angle used was 30°. For such experimental conditions the depth resolution at the surface should be on the order of 500 Å[12]. Any abrupt changes in the depth profile are going to be broadened when observed at this depth resolution. On the other hand, for a depth profile where the change is rather gradual over a distance of hundreds of ångstroms, the FRES will provide an accurate measurement. Thus, FRES is useful in discerning whether small amounts of the diffusant have penetrated deeply into the sample.

RESULTS

The NR results from 27 000 g mol^{-1} DPS experiments are given in *Figure 1a* with the corresponding real-space depth profiles shown in *Figure 1b*. In *Figure 1a* the fitted reflectivity result (solid line) is given together with the experimental data (discrete symbols). After 2 h of annealing at 133°C most of the DPS chains diffused into the network and only a minor amount was left behind, that is, along the silicon/polymer interface. After annealing, there is no clear indication in the fits of a steep drop in the DPS concentration at the DPS/XHPS interface, even though this scenario was tried as a possible fit to the data. However, the 30 min result of *Figure 1b* seems to give some hint of a step. The NR results of 10 500 and 90 000 g mol^{-1} DPS are qualitatively similar to the 27 000 g mol^{-1} DPS data, albeit with different diffusion coefficients, and are not shown.

The results for 401 000 g mol^{-1} DPS experiments are given in *Figure 2*. From the reflectivity curves (*Figure 2a*) there are two important features worth noting: (a) the changes in the reflectivity slow down conspicuously after 45 min at 162°C even though the annealing time was incremented by a factor of two between subsequent runs, and (b) the periodicity of the interference fringes does not change upon annealing. For clarity only the first three fitted reflectivity results (solid line) are given together with the experimental data (discrete symbols). The fitted results of 105 and 285 min closely resemble the fit to the data taken after only 45 min of annealing. The corresponding results in real space (*Figure 2b*) further substantiate the observation that the Q_c^2 profile inside the XHPS reached its final shape after 45 min of annealing. The thickness of the DPS film remained unchanged despite a continuous decrease in Q_c^2 within the DPS thin film region. This decrease provides an unequivocal evidence of the diffusion of linear chains out of the film. In *Figure 2b*, the result of the sample before annealing indicates the existence of an air gap at the DPS and XHPS interface where its Q_c^2 reaches zero over a narrow region of about 50 Å in width. Presumably the 90°C pre-annealing temperature did not always heal the gap between the DPS and XHPS blank. A steep drop off in the DPS concentration at the DPS/XHPS interface, that is, at the diffusion front, was observed for all the samples after being annealed at 162°C. The NR data cannot otherwise be fit accurately without including this characteristic steep drop in the composition profile. The observation of an invariable DPS film thickness will be the subject of further discussion.

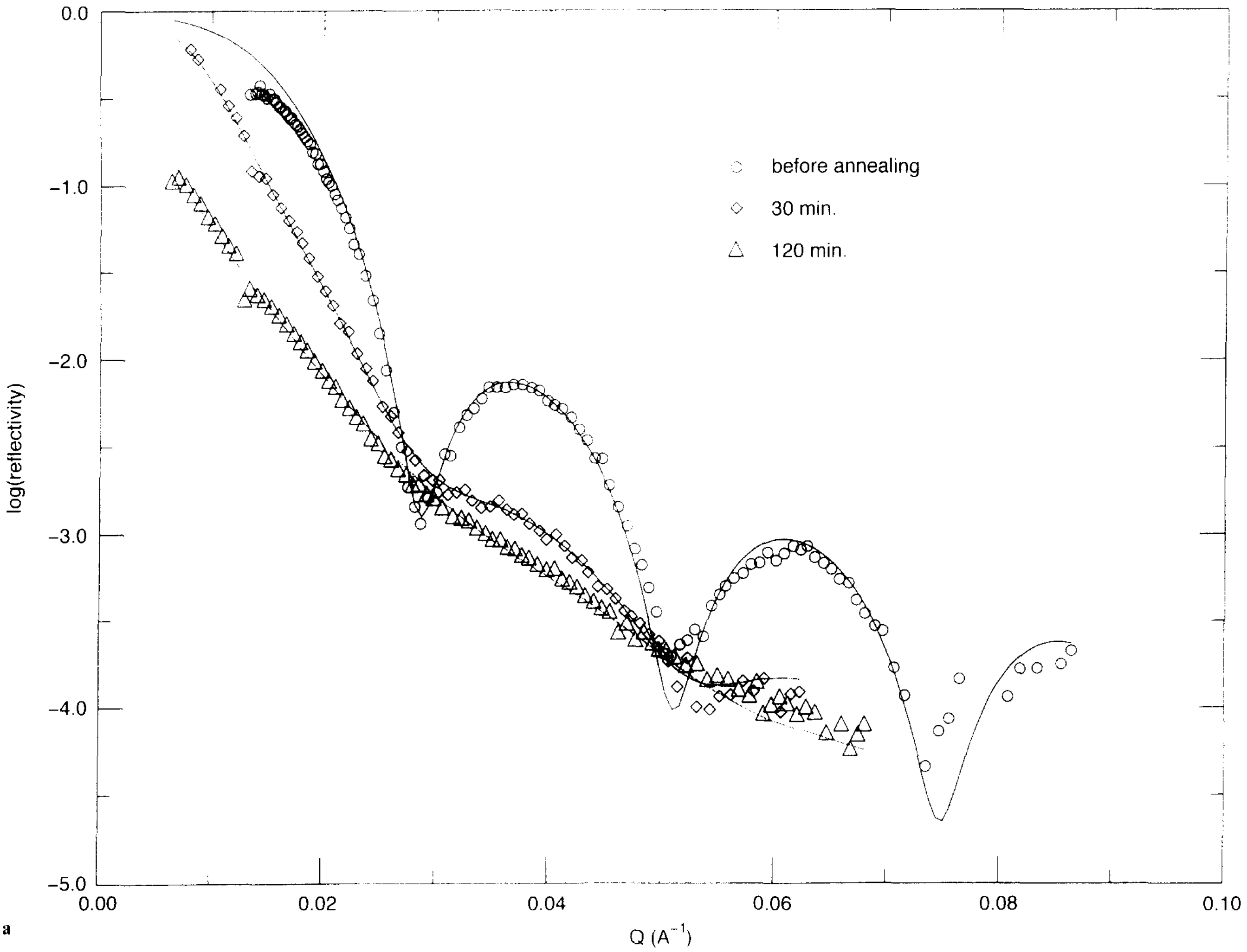

Figure 1 (a) Neutron reflectivity (NR) results from 27 000 g mol^{-1} deuterated polystyrene diffusing into crosslinked hydrogenated polystyrene (XHPS). The experimental data are shown as discrete symbols and the best fits are presented as solid lines. The abscissa is given in amplitude of the scattering vector, $Q = (4\pi/\lambda)\sin\theta$, where θ is the grazing angle of incidence. The annealing temperature was 133°C and the initial film thickness was 257 Å. Results from three different annealing times are presented. (b) Concentration profiles of deuterated polystyrene (DPS) derived from fitting the NR results of (a). The abscissa is depth in ångstroms with the silicon/DPS interface near the origin and the DPS/XHPS interface near 270 Å. The ordinate is given in terms of the elastic scattering length per unit volume, Q_c^2, which is linearly proportional to deuterium concentration. The Q_c^2 values for DPS, HPS and silicon are 3.25×10^{-4}, 7.1×10^{-5} and 1.06×10^{-4} Å^{-2}, respectively

The NR results from 690 000 g mol^{-1} DPS experiments are qualitatively similar to those of the 401 000 g mol^{-1} DPS experiments. The reflectivity keeps on diminishing with annealing time (*Figure 3a*) while the periodicity stays almost unchanged. For clarity, in *Figure 3a* the fitted reflectivity results of the 30, 60 and 180 min are the only ones given. The corresponding Q_c^2 profiles (*Figure 3b*) again suggest a sharp drop off at the DPS/XHPS interface together with a nearly invariable DPS profile inside the XHPS. (Note that each of the Q_c^2 profiles from different annealing times in *Figure 3b* was shifted horizontally by 30 Å from one another for clarity.) Note that in *Figures 1a, 2a* and *3a* the NR data statistics reach an undesirable stage once the reflectivity goes below 10^{-4}, this is equivalent to the Q region beyond 0.06 Å^{-1}.

In order to examine the significance of the sharp drop in the Q_c^2 profile at the polymer interface, the profile of the 690 000 g mol^{-1} DPS sample, which shows the sample annealed for 60 min, was modified to eliminate the sharp drop as shown in *Figure 4a*. Such a minor modification results in a significant change in reflectivity especially in the high Q region, as illustrated in *Figure 4b*. The above comparison was made using data within $Q < 0.06$ Å^{-1} showing that data in this Q-range is sensitive to sharp drops in the concentration profile. The fit between the measured (solid circle) and the fitted (solid line) reflectivity results is rather poor in the Q region greater than 0.03 Å^{-1}, that is, the experimental data exhibit deeper oscillations than the calculated fit. By smoothing the sharp transition at the polymer interface, the oscillation in the calculated NR is severely damped in this high Q region, and provides a less satisfactory fit to the data.

There is another salient feature in *Figure 3b* worth noting: there is a broadening of the DPS/silicon interface as annealing proceeds. This observation suggests an increasing presence of the hydrogenated sol molecules at this interface. This is a reasonable idea since low molecular weight species are known to accumulate at such interfaces.

The 690 000 g mol^{-1} DPS sample of *Figure 3* was later analysed with FRES. After NR measurements, when the sample was returned to room temperature, due to their high thermal shrinkage the XHPS blank always debonded from the silicon wafer. The debonding occurred along the DPS/silicon interface and left a clean silicon surface. The resultant DPS/XHPS blanks

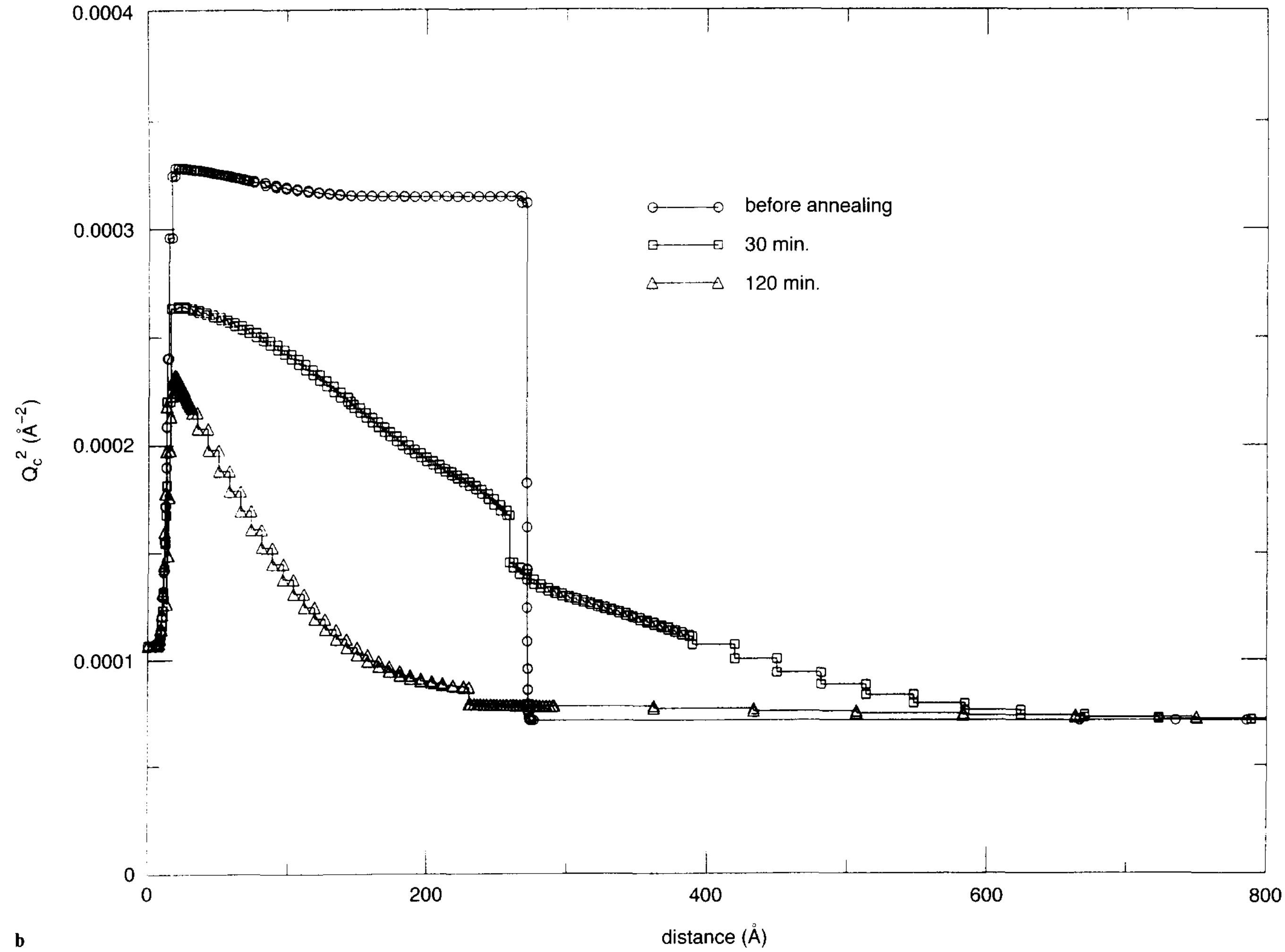

Figure 1 Continued

could then be examined by ion scattering. The FRES results indicated that the entire DPS film was intact and had remained localized at the interface. This observation implied that (a) after 840 min at 174°C the DPS layer was securely bonded to the XHPS because the debonding must have taken place neatly along the silicon/DPS interface, and (b) all the 690 000 g mol^{-1} DPS chains are still located at the polymer interface (within the 500 Å spatial resolution of the FRES measurement). In other words, no long range diffusion had taken place.

The remainder of FRES results described were collected from samples specifically prepared for ion scattering using the procedure described in the sample preparation section.

The FRES results for the 690 000 g mol^{-1} DPS sample annealed at 174°C for 30 min, and subsequently at 160°C for 6.5 h, are given in *Figure 5*. Here the deuterium scattering yield, which is proportional to the amount of deuterium in the sample, is plotted against the kinetic energy of scattered deuterium, which scales with depth into the sample, with lower energies corresponding to greater depths. No significant change is observed in either the peak height or the peak shape. This observation is consistent with that of the NR results shown in *Figure 3b* where the Q_c^2 profiles also suggest no long range diffusion up to 840 min at 174°C. The NR results indicated that diffusion has occurred up to 200–300 Å into the XHPS but did not change much with additional annealing time. That is, the DPS layer had not decreased in thickness even at long annealing times. This is in contrast to the NR results and subsequent FRES measurements. Each showed substantial diffusion of the 27 000 g mol^{-1} DPS into the XHPS with the FRES showing diffusion on the order of several thousand ångstroms.

The FRES results of 401 000 g mol^{-1} DPS are given in *Figure 6a* with an enlarged area of the deuterium peak given in *Figure 6b*. Diffusion of the linear DPS proceeded to near completion as judged from the disappearance of the deuterium peak height after annealing for 5 h. This is quantitatively different from the NR results of *Figures 2a* and *b*. The NR results indicated that over half of the DPS remained within the thin film region after subjecting to a similar annealing condition. It seems that the diffusion was retarded somewhat in NR samples in comparison to FRES samples. This type of quantitative difference between NR and FRES results is believed to be caused by the difference in the sample configurations instead of by differences in the measurement techniques. For NR samples, one side of the DPS film was adhered to a silicon wafer while in the FRES samples the corresponding side of the DPS film was exposed to vacuum. The adhesion between silicon wafer and DPS layer is expected to slow down the diffusion process[13]. In this work we merely acknowledge this difference; a detailed discussion on substrate effects will be given elsewhere.

A particular feature in the FRES experiments shown in *Figure 6b* is worth noting: the deuterium peaks of

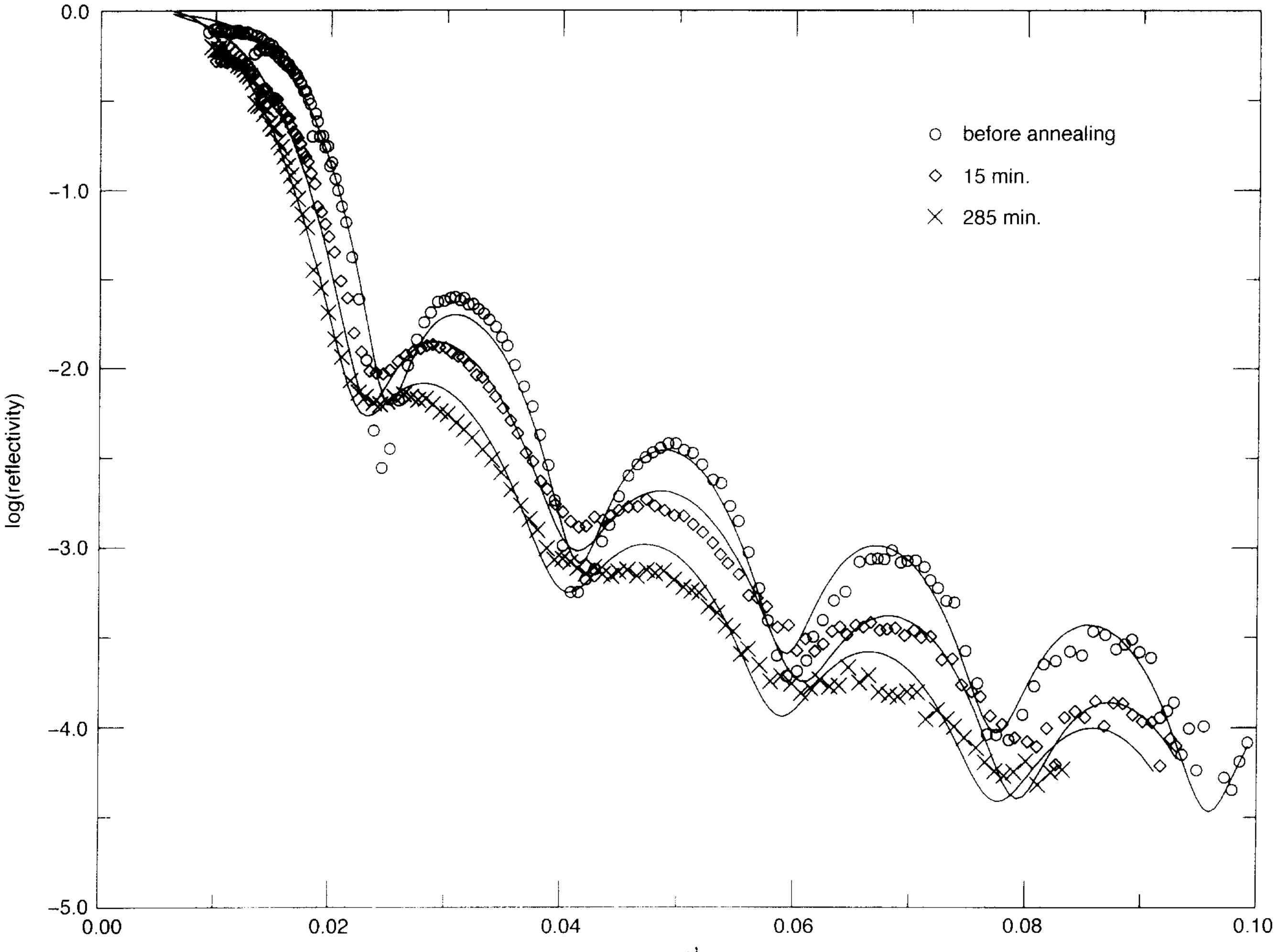

Figure 2 (a) Neutron reflectivity (NR) results from 401 000 g mol^{-1} deuterated polystyrene (DPS) into crosslinked protonated polystyrene (XHPS). The experimental data are shown as discrete symbols and the best fits of the first three data sets are presented as solid lines. The annealing temperature was 160°C and the initial film thickness was 330 Å. Results from three different annealing times are presented. (b) Concentration profiles of deuterated polystyrene derived from fitting the NR results of (a). The abscissa is depth in ångstroms with the silicon/DPS interface near the origin and the DPS/XHPS interface near 350 Å. The ordinate is given in terms of the elastic scattering length per unit volume, Q_c^2, which is linearly proportional to deuterium concentration

samples annealed for 15 min, 30 min and 2 h have similar, overlapping profiles on the low-energy side (channels 260–320). This suggests that the DPS concentration profiles inside the XHPS at those three specific conditions were similar and stayed unchanged with annealing time. The corresponding NR results (*Figure 2b*) are also consistent with this notion. This observation provides strong real-space evidence supporting a limited solubility of linear DPS within the XHPS. As to the DPS chain content within the thin film region, we observed a steady decrease with annealing time evident from a progressive decrease in the peak height of the high energy side of the deuterium peak in both *Figures 6a* and *b*. This is also consistent with the NR results.

DISCUSSION

A central observation of this work is the manifestation of a persistent sharp drop in the composition profile at the DPS/XHPS interface for the 401 000 and 690 000 g mol^{-1} DPS samples even after extended annealing times. This drop is due to the limited solubility of these high molecular weight linear DPS molecules in the crosslinked matrix. The extreme abruptness of the interfaces makes it difficult to observe by any method other than NR. This may explain why this observation, though expected, has not been more widely reported. Another explanation for why this observation is not more widely reported may be found in the possibility of capillary waves whose existence has been used to explain why sharp interfaces, when searched for with NR, were not discovered[14]. However, in the present experiments capillary waves are not expected to play a prominent role in interface broadening owing to the proximity between the polymer/polymer interface and the silicon surface which is mediated only by the thin linear DPS layer on the order of 300–500 Å thick. The anchoring of this DPS layer to the silicon surface is expected to dampen any capillary waves. This, in turn, leads to the sharp interfaces that were observed experimentally. In ref. 14 the interface examined by NR was many thousands of ångstroms away from the silicon substrate. In such cases capillary waves are expected to play an important role in interfacial thickness as observed by any measuring techniques sampling a wide area.

Perhaps the most striking result encountered is the invariance of the DPS film thickness with annealing time as revealed by the NR results of the 401 000 and

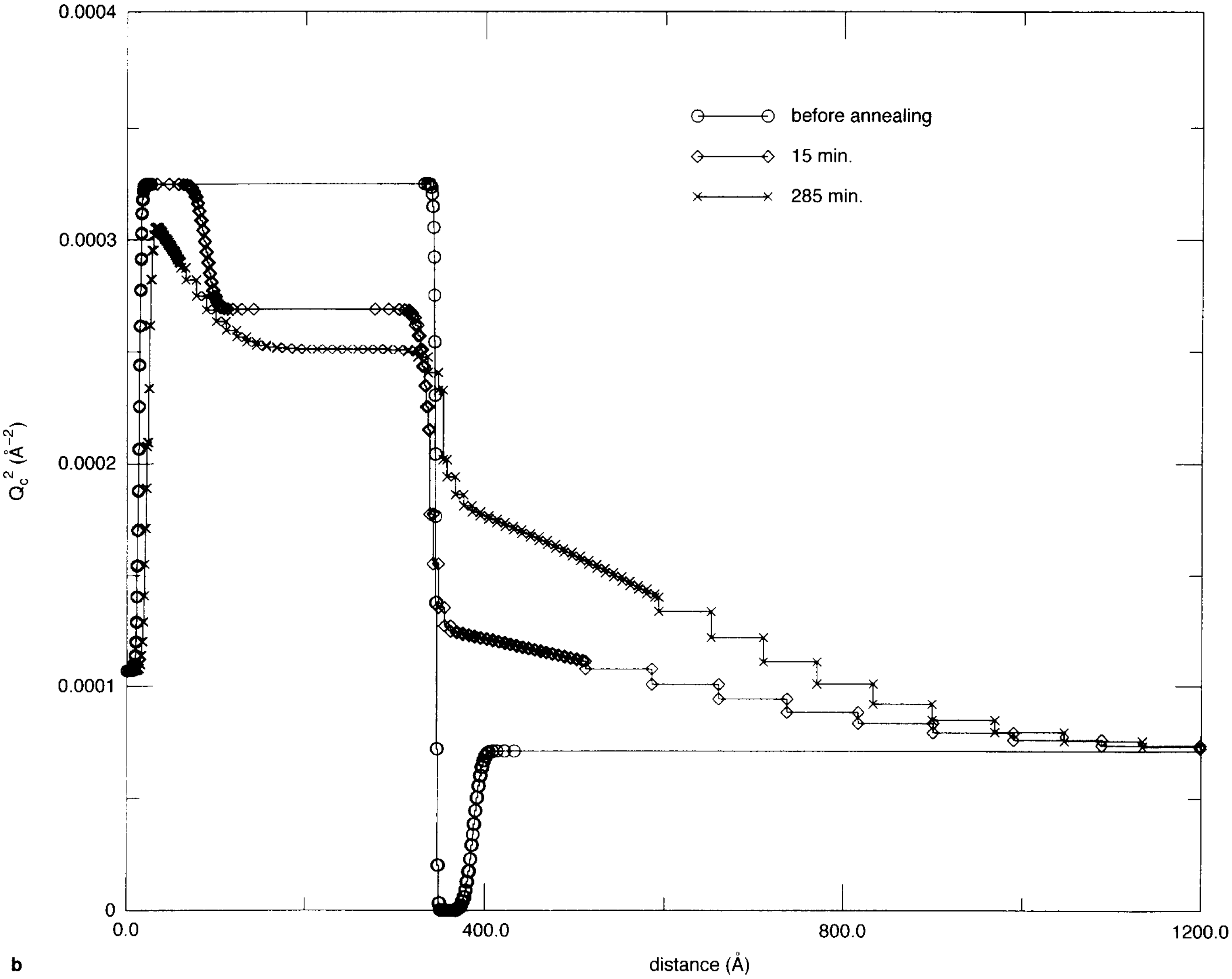

Figure 2 Continued

690 000 g mol^{-1} DPS samples. This invariance was observed even though both the NR and the FRES results indicated that a certain amount of DPS had already diffused out of the thin film region into the XHPS. Based on the concept of conservation of mass, the counter diffusion of hydrogenated species from the XHPS must match the volume of the lost DPS chains. As mentioned previously, the sol content of the XHPS used in this work was found to be about 2%. The thickness of the XHPS is 2 mm while the DPS film thickness is 300–500 Å, even at this low sol concentration there will always be sufficient sol molecules for counter diffusion to compensate the loss of DPS. The question that immediately follows is: why does the counter diffusion of sol exactly balance the DPS diffusion, such that the original thickness of the DPS film was preserved? This can also be stated differently. Why is there *no swelling in the XHPS* as judged from the position of the DPS/XHPS interface which stayed unchanged with respect to the DPS/silicon interface?

The equilibrium swelling ratio of polymer network by linear chains can be calculated within the context of the Flory–Rehner theory. Explicitly, equation (3) relates the equilibrium swelling $1/\phi$ with the linear chain molecular weight n_l, the molecular weight between crosslinks n_c, the Flory–Huggins interaction parameter χ between the network chains and linear chains, and the volume fraction ϕ_s of network chain during crosslinking. Note that both n_l and n_c are expressed in terms of degree of polymerization.

$$-\frac{\phi_s^{-2/3}}{n_c}\phi^{-5/3}+\frac{1}{2n_c\phi}-\chi-\frac{1}{\phi n_l}\left(1+\ln(1-\phi)+\frac{1-\phi}{\phi}\ln(1-\phi)\right)\left(1+\frac{\ln(1-\phi)}{\phi}\right)=0 \qquad (3)$$

The value of χ was taken as $-2.9\times10^{-4}+0.2/T$ for the DPS and HPS pair[15], where T denotes temperature in degrees Kelvin. If one lets ϕ_s be unity, since the crosslinking took place in bulk, the value of ϕ can be calculated easily as a function of n_l. The calculated results of 150°C are given in *Table 1*.

These results indicate that the solubility of linear chains inside networks depends strongly on n_l for a given n_c. For the present case of $n_c = 22\,000$ g mol^{-1}, the solubility is negligibly small when n_l is equal to or above 401 000 g mol^{-1}. Within the test temperature range of 130–170°C this solubility does not change significantly. This can be understood since the value of χ is small and depends only weakly on temperature. Qualitatively this calculation indicates that the gain in entropy from the diffusion of DPS chains is too small to compensate for the increase in elastic energy from network swelling.

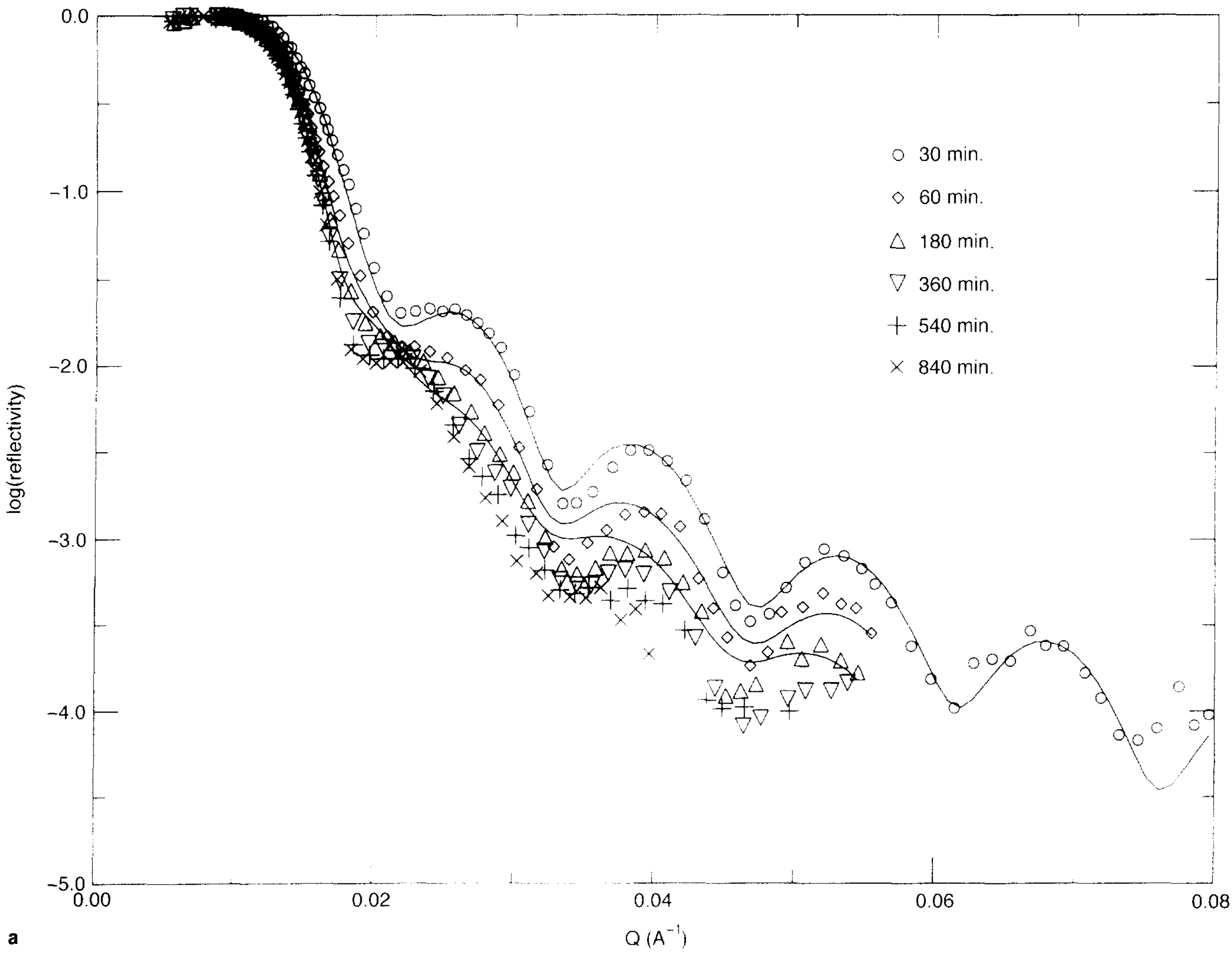

Figure 3 (a) Neutron reflectivity (NR) results from 690 000 g mol^{-1} deuterated polystyrene (DPS) into crosslinked protonated polystyrene (XPS). The experimental data are shown as discrete symbols and the best fits of the first three data set are presented as solid lines. The abscissa is given in amplitude of the scattering vector, $Q = (4\pi/\lambda)\sin\theta$, where θ is the grazing angle of incident. The annealing temperature was 174°C and the initial film thickness was 420 Å. Results from six different annealing times are presented. (b) Concentration profiles of deuterated polystyrene derived from fitting the NR results of (a). The abscissa is depth in ångstroms with the silicon/DPS interface near the origin and the DPS/XHPS interface after 30 min annealing near 470 Å. *For clarity, the profiles for the subsequent measurements were shifted horizontally by 30 Å from one another.* The ordinate is given in terms of the elastic scattering length per unit volume, Q_c^2, which is linearly proportional to deuterium concentration

In other words, the network will stay unswollen if the diffusant molecular weight is greater than 401 000 g mol^{-1}. There was a second factor further limiting the solubility of linear chains: the swelling of network chains parallel to the interface was constrained by the silicon wafer. The network was allowed to swell only in the direction normal to the interface. Thus, the only possible diffusion process is a balanced counter-diffusion between the XHPS sol molecules and the DPS chains, thereby the network chains experience a negligible disturbance during this equal-volume exchange between the two mobile species.

The above calculation is valid for bulk materials since no surface or interface is included. It has been well established that the free energy of interfaces and surfaces depends not only on their local composition but also on the composition gradient[16]. More explicitly, the free energy increases as the second power of composition gradient. In general, this square gradient contribution tends to smooth out any abrupt changes across interfaces because a steep change in composition, i.e. a large gradient, results in an increase in free energy. Accordingly, the DPS concentration is expected to be enhanced somewhat near the interfacial region over its bulk values given in *Table 1*. However, if one maintains that the degree of swelling of polymer networks is *finite*, that is, with an upper limit simply caused by the fact that the chains between crosslinks cannot be extended beyond their contour length, one still expects to observe a steep drop in DPS concentration at the diffusion interface. Across the interface the DPS concentration changes from that of the thin DPS film to this finite solubility limit. The width of this interface is expected in the range of the radius of gyration of the crosslinked chain, or about 40 Å.

Table 1 Calculated equilibrium deuterated polystyrene (DPS) concentration within a hydrogenated polystyrene network (XHPS) with a molecular weight of 22 000 g mol^{-1} between crosslinks

DPS molecular weight (g mol^{-1})	690 000	401 000	90 000	27 000	10 500
Equilibrium content (vol%)	~0	0.00002	0.042	0.24	0.45

One intrinsic assumption of the above calculation using the Flory–Rehner equation is that the conformation of the linear diffusant chains stays unchanged

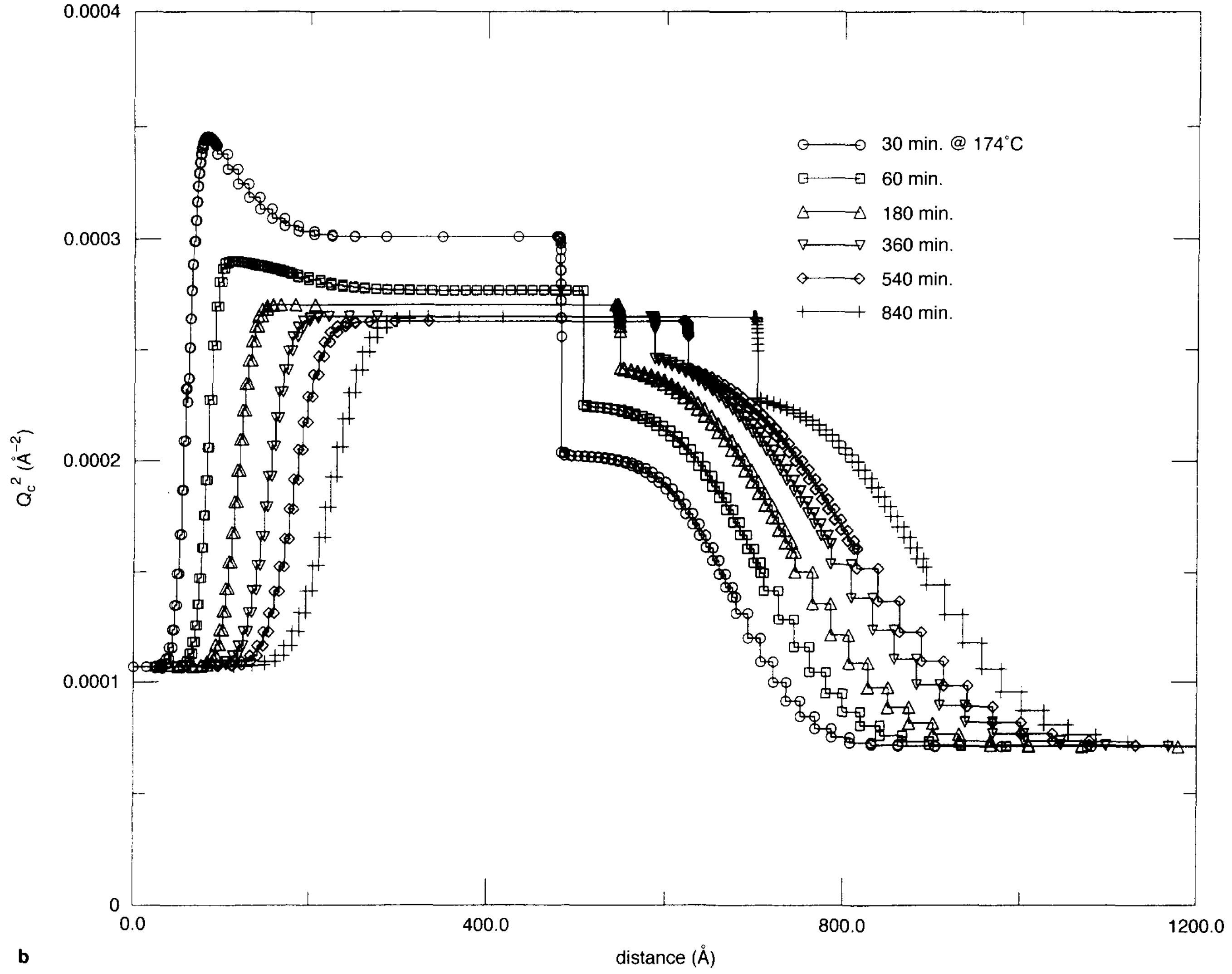

Figure 3 Continued

whether inside the XHPS or in the DPS bulk phase. Recent experimental findings seemed to suggest some contraction of linear chains inside a network[17,18]. If confirmed, this contraction will further decrease the solubility limit since additional elastic energy will arise from the diffusant chain contraction.

In order to avoid the complicating factor of sol counter diffusion, attempts were made to extract the sol from the XHPS by using solvents. However, extraction invariably resulted in rough surfaces no longer suitable for NR study.

For the 401 000 g mol^{-1} DPS sample beyond 15 min annealing time, the DPS concentration inside the XHPS near the polymer/polymer interface (*Figure 2b*) is about 50% by volume as given by its Q_c^2 value of 0.00017. It is believed that such a high concentration of DPS does not imply a high local swelling due to the square gradient contribution, rather, it likely reflects the local concentration of the sol even though the average sol content throughout the XHPS was found to be about 2%. A swelling of the XHPS near the interface will result in a decrease of the DPS film thickness but this is not observed experimentally. The sol concentration within a few hundred ångstroms from a free surface of a free radical cured XHPS sample could be substantially greater than its bulk average. The Q_c^2 or deuterium profiles within the XHPS from both NR and FRES (*Figures 2b*, *3b* and *6b*), therefore, does not necessarily represent a diffusant concentration profile predicted from any diffusion theory considering a uniform diffusion medium. The spatial distribution of sol can compound these Q_c^2 or deuterium profiles significantly. The apparent difference in the DPS concentration at the DPS/XHPS interface between *Figures 2b* and *3b* is likely caused by the sample to sample variation in their near surface sol content.

The discrepancy between the FRES (*Figure 6b*) and NR (*Figure 2b*) results has also been observed on samples with 90 000 g mol^{-1} DPS: the diffusion was more rapid in FRES samples than in NR samples. The presence of a solid substrate onto which the DPS chains were spin coated seems to have retarded the diffusion process. This phenomenon has been observed by others[13] on the study of linear PS interdiffusion. The attraction between the DPS and the silicon substrate is believed to be the cause. In most of the Q_c^2 profiles presented in this work, it is noticeable that the DPS concentration near the substrate (the origin on the abscissa of those figures) was higher than the rest of region. This observation is consistent with the notion that some DPS chains were attracted to the silicon substrate. The only exception can be found in 690 000 g mol^{-1} DPS result of *Figure 3b* where a

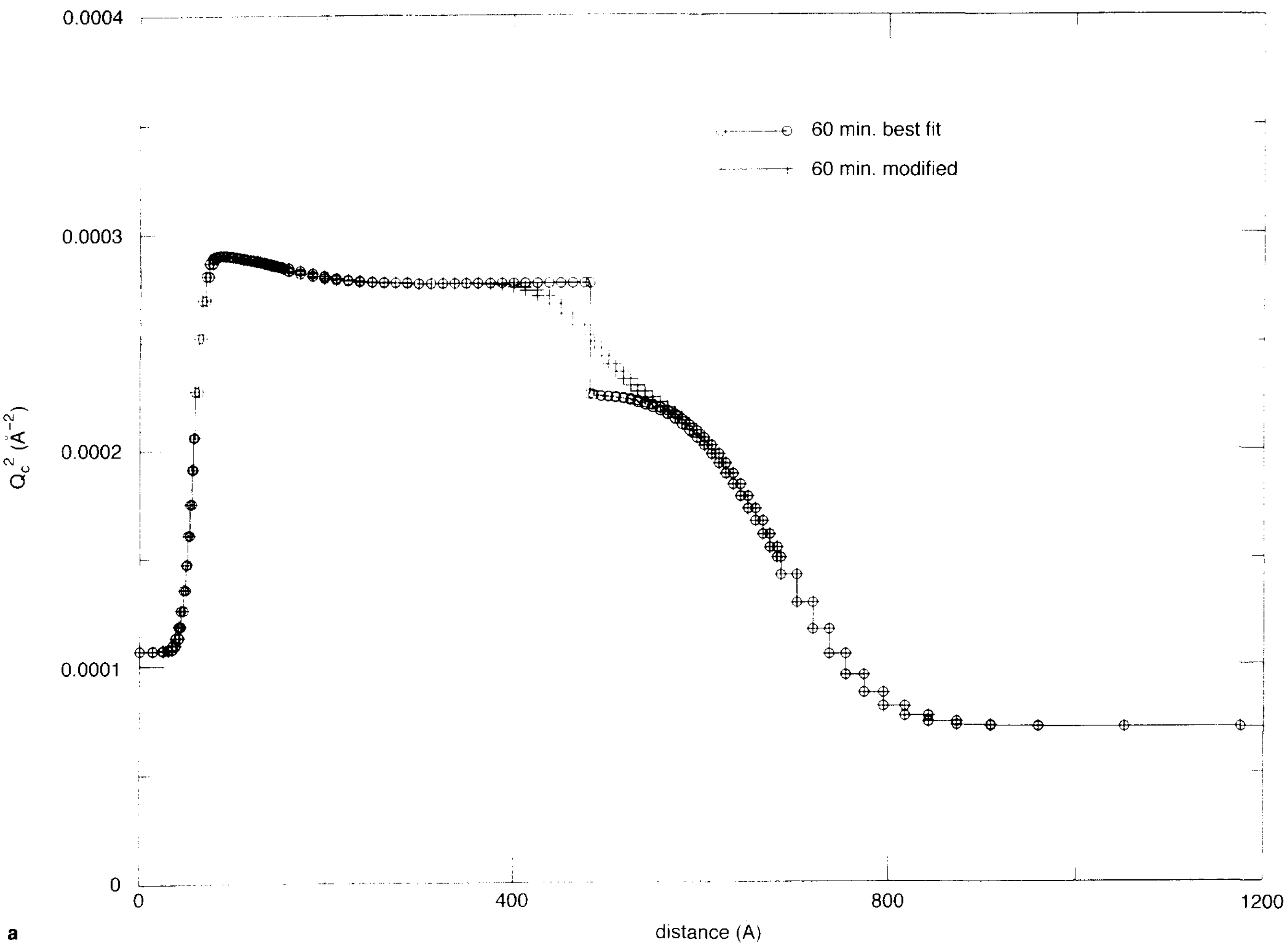

Figure 4 (a) Concentration profiles of deuterated polystyrene of 690 000 g mol^{-1} sample after being annealed at 174°C for 60 min (○). A modification was made on the above profile to remove the steep drop at the DPS/XHPS interface (×). (b) Experimental neutron reflectivity (NR) results (○) of the 690 000 g mol^{-1} DPS sample after being annealed at 174°C for 60 min. The corresponding NR result calculated from the best fit profile of (a) is shown together with the one calculated from the modified profile. Note the one from the modified profile lacks the oscillations of the experimental data in the region of $Q > 0.03$ Å^{-1}

depletion of DPS is present near the DPS/silicon interface after 360 min of annealing at 174°C. As mentioned previously, this could be caused by the accumulation of sol molecules from XHPS block. The discrepancy between the FRES results of 401 000 (*Figure 6b*) and 690 000 DPS (*Figure 5*) is rather troublesome. This result tends to suggest that there is a sharp decrease in diffusion coefficient between these two molecular weights. Note that both these molecular weights are far above that of the network molecular weight. Such a sharp cut-off is unexpected, more experiments need to be done to clarify this point.

As for the 690 000 g mol^{-1} DPS samples, both the FRES and the NR results indicate that the diffusion occurred only within a surface region of a few hundred ångstroms. The DPS chains, although penetrating into the surface layer which presumably contained more sol, never diffuse deeply into the bulk. This observation indicates the existence of an upper limit in the diffusant molecular weight beyond which diffusion ceases to occur. The dependence of this upper limit on n_c is the subject of an on-going study.

The sensitivity of NR to certain details of the Q_c^2 profile is demonstrated in *Figures 4a* and *b*. However, the NR results are not sensitive to the length or the detailed shape of the diffusion tail far away from the DPS/XHPS interface. Therefore, there is no attempt to examine the validity of the conservation of DPS mass in all the best-fitted NR results. Mass conservation requires the total area underneath the Q_c^2 profile to remain unchanged.

CONCLUSION

Neutron reflectivity results have confirmed the presence of a sharp drop-off in DPS concentration at the DPS/XHPS interface. This drop-off, observed most prominently at molecular weights 401 000 and 690 000 g mol^{-1}, was ascribed to the limited solubility of these high molecular weight linear polymers in the tightly crosslinked HPS network. It took the high resolution of NR to detect this sharp concentration profile. Other attempts to measure this effect may have failed due to a lack of depth resolution, or to the presence of capillary waves at the interface being studied.

Forward recoil scattering experiments, used to corroborate the NR results, indicated that linear DPS of 690 000 g mol^{-1} would not diffuse into HPS network with a 22 000 g mol^{-1} crosslink molecular weight even after long periods of annealing. NR results, however, indicated that some interpenetration has indeed occurred within a few hundred ångstroms of the DPS/XHPS

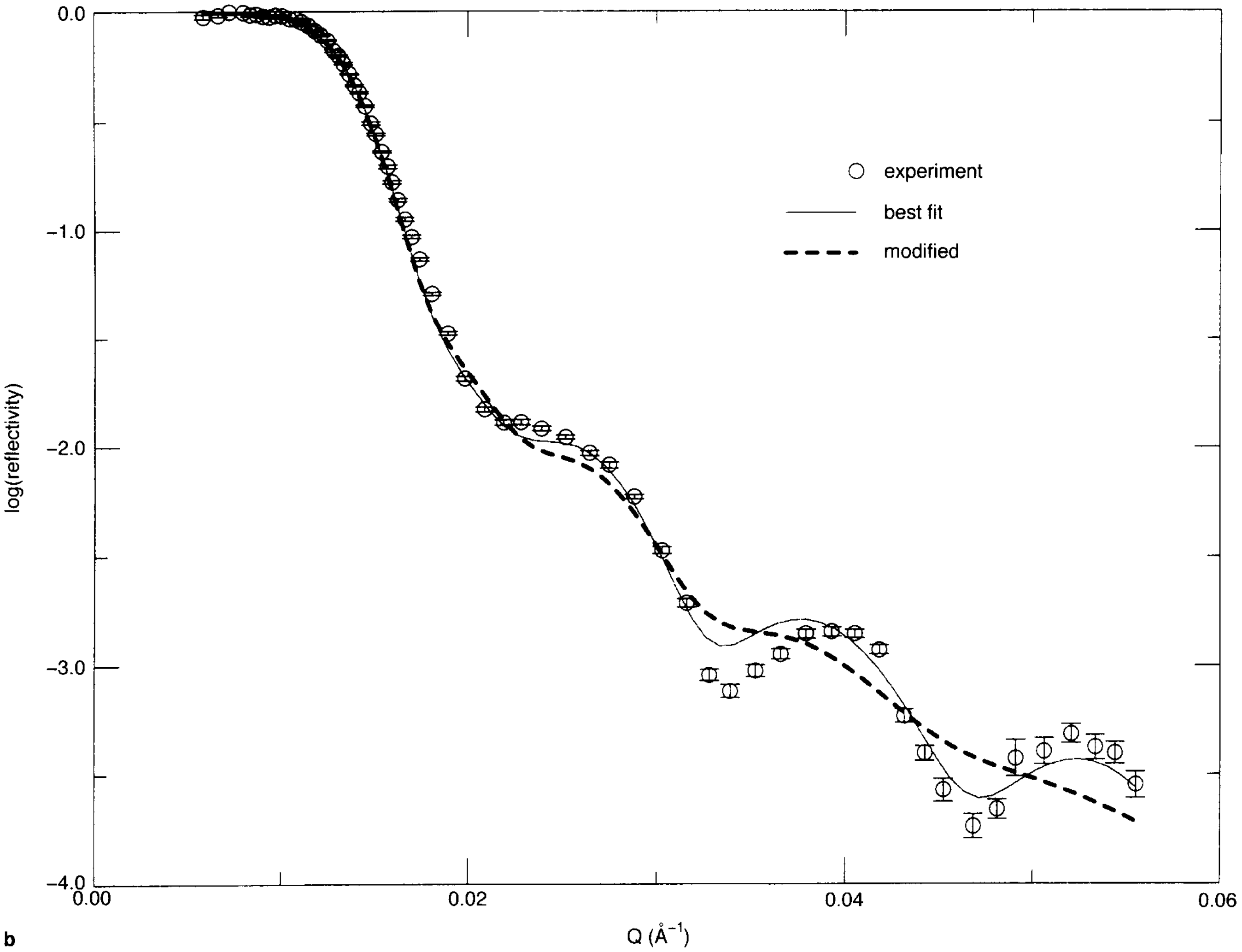

Figure 4 Continued

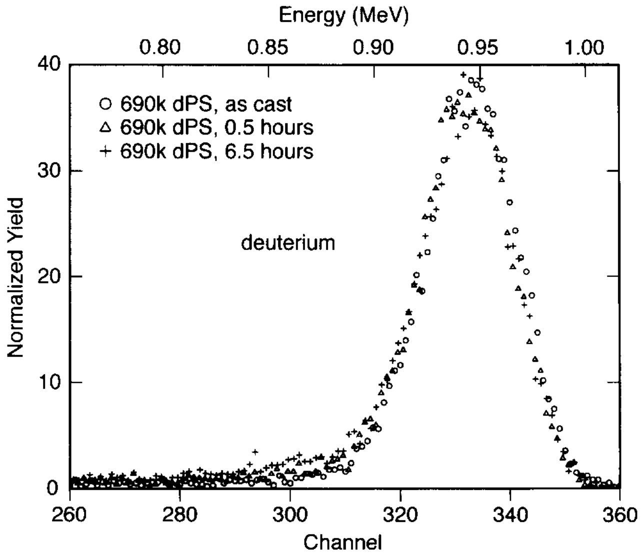

Figure 5 Forward recoil scattering (FRES) results for 690 000 g mol^{-1} DPS samples corresponding to an as-cast sample (O), annealed at 170°C for 30 min (△) and annealed at 160°C for 6.5 h (+). The data indicate a barely detectable level of diffusion of the DPS into the XHPS

interface but that no further diffusion into the cross-linked material was observed even after the extended annealing times. For 401 000 g mol^{-1} linear DPS, long range diffusion was confirmed by FRES measurements while NR results indicated only a short range diffusion confined within a few hundred ångstroms from the interface. A similar difference between FRES and NR results was also observed in the 90 000 g mol^{-1} DPS experiments. Diffusion in samples prepared for FRES was always faster than those prepared for NR. The difference in sample geometry between FRES and NR is believed to be the cause of this observed discrepancy. The presence of a silicon wafer at the back side of the linear DPS layer in the NR samples tended to retard the diffusion process somewhat.

Between the high molecular weight linear DPS and the HPS network, the diffusion process is believed to be balanced by counter diffusion of sol molecules from the network. Such a diffusion process does not invoke the swelling of the network. The presence of a steep drop of DPS concentration inside the XHPS can be accounted for by this diffusion process. This diffusion process is also in agreement with a calculated result using Flory–Rehner theory. The equilibrium swelling of a network by linear chains with molecular weights in the range considered in this work is negligible. Based on this counter diffusion process, the local diffusion of high molecular weight DPS into XHPS in the interface region

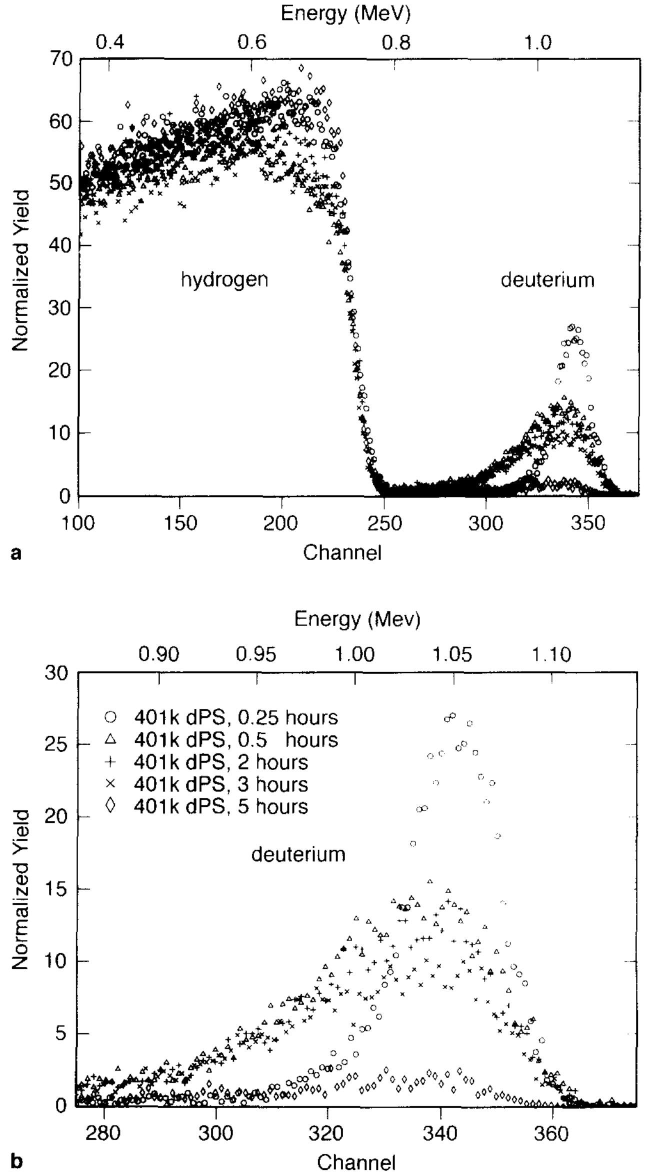

Figure 6 (a) FRES results for 401 000 g mol^{-1} DPS samples annealed at 160°C corresponding to times of 15 min (○), 30 min (△), 2 h (+), 3 h (×), and 5 h (◇). The data correspond to a real space concentration profile with deuterium diffusion occurring toward the left, that is, toward lower channel numbers. The data for 30 min, 2 h and 3 h overlap on the low energy side (channels 280–320) corresponding to the same deuterium concentration profile at the DPS/XHPS interface, while the concentration in the DPS overlayer (channels 320–360) continuously decreases. This suggests that there is a limited solubility of DPS in the XHPS leading to an unchanging concentration profile near the interface at intermediate annealing times. (b) An enlarged view of (a) showing the deuterium profile in the region of the DPS/XHPS interface

may only reflect a high sol concentration near the surface of the XHPS blanks.

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