The diffusion of salt solutions into nylon-6

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The transport kinetics and concentration profiles of zinc chloride and lithium bromide into nylon-6 have been investigated. Polymers were soaked in solutions of known concentration for varying lengths of time, and cross-sectional analysis of each sample was then carried out using the energy dispersive X-ray (EDA) technique, supplemented by microprobe (wavelength dispersion, WDA) and atomic absorption data. Broad agreement was obtained between EDA and WDA techniques when depth of penetration and concentration profiles were measured on the same samples, and estimates of salt concentrations in nylon were similar for both the WDA and atomic absorption methods. When the concentration of aqueous zinc chloride solution was increased, a transition from anomalous to Case II behaviour was observed: an abrupt increase in uptake as salt concentration approached 4 M was also observed. Lithium bromide transport was poorly defined by comparison, in keeping with a different mechanism of association to the polymer. Adoption of EDA and WDA methods should facilitate future progress in the study of diffusion characteristics of polymers.

Keywords Diffusion; sorption; nylon; zinc chloride; lithium bromide; X-ray analysis

INTRODUCTION

It has been established for some time that the diffusion of a liquid penetrant into a polymer can proceed according to one of two district processes, known as Case I and Case II diffusion[1]. In Case I behaviour the Fickian equations are obeyed and intially the total absorption (x) of the penetrant obeys the equation

$$x = Kt^{\frac{1}{2}}$$

where K is a constant and t the time.

With Case II diffusion a front is formed between the swollen and unaffected polymer which advances into the interior[2,3] at a constant rate leading to a relation of the type

$$x = K't$$

Between these two limiting cases 'anomalous' diffusion may occur where

$$x = Kt^n$$

with $\frac{1}{2} < n < 1$[4].

Many penetrants show all types of behaviour depending upon temperature and penetrant activity[5]. For example, Stannett[6] and coworkers have shown that a changeover from Case I to Case II behaviour in polystyrene takes place as the activity of n-pentane penetrant is increased. Furthermore, Windle and Thomas[7] showed that the Case II transport of methanol in PMMA could change to Case I when the temperature was raised.

The above work had been carried out with organic penetrants mainly in amorphous polymers. Andrews[8], however, has studied the penetration of of aqueous zinc chloride solutions in nylon-6 and found specific effects of salt concentration upon crystallinity. The interest associated with these effects is increased because nylons are subject to cracking in salt solutions. For example, Dunn and Sansom[9] found that with aqueous zinc chloride solutions the time for cracking was dramatically reduced as the concentration was increased from 30% w/v (2.2M) to 50%. Highly localized plastic deformation was found on fracture surfaces of nylon-6 cracked by zinc chloride, by Reimschussel and Kim[10]. However, on the basis of comparison between the rapid swelling behaviour of finely powdered nylon-6 with the relatively unswollen thick sheet ($\geqslant$ 1.5 mm), they concluded that zinc chloride was a good plasticizer for nylon-6 but had a very low diffusion coefficient, leading to weak craze formation. Indeed extensive crazes have been reported for both 'bulk' nylon-6[11,12] and nylon-6,10 films[13].

In order to widen the basis of diffusion studies and to provide a further background for the understanding of cracking processes we have now investigated the penetration of zinc and lithium halides (both powerful stress cracking agents, but with differing modes of action[9,12]) mainly in nylon-6.

The problem of measuring the penetrant concentration at different distances from the polymer: penetrant interface was solved by Thomas and Windle[7] by using iodine (as a visual aid) in the methanol penetrant. Although they obtained important results this method would be less successful for studies in the more opaque nylons; further, crystallographic changes are known to occur in nylons with iodine/potassium iodide solutions[8].

In the case of nylon-6 zinc chloride we have now been able to measure the penetrant directly by means of scanning electron microscopy together with energy dispersive X-ray analysis (EDA). Concentration-displacement data have been obtained over the period of the experiments, and are compared with results obtained

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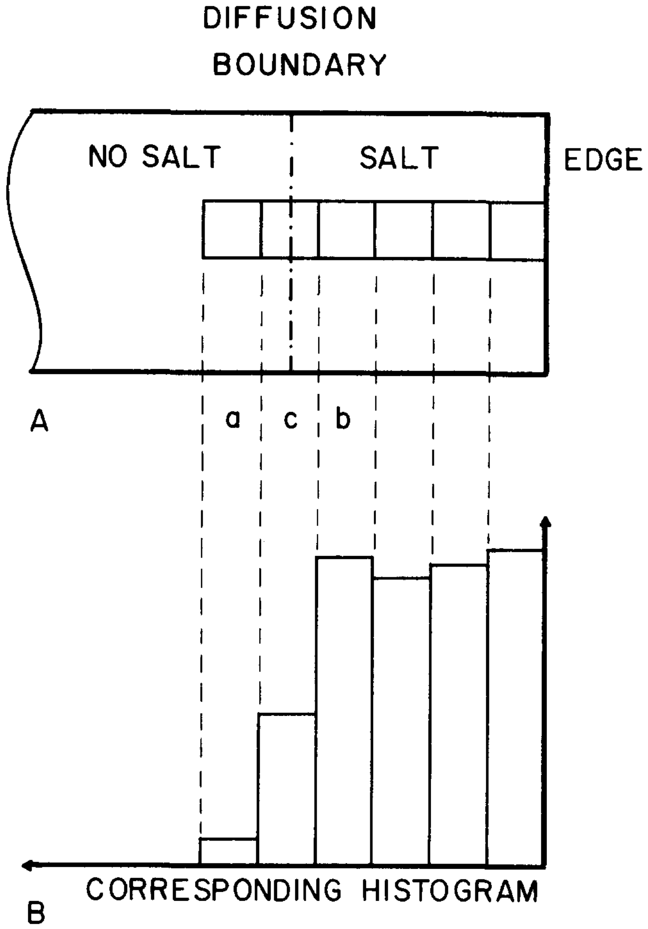

Figure 1 Energy dispersive analysis, using step method to obtain histogram

by wavelength dispersive X-ray analysis as well as atomic absorption data from microtomed slices of the treated polymer.

EXPERIMENTAL

Materials

Two polymers, nylon-6 and nylon-6,6, were employed in all experiments. The nylon-6 sample was found to have a viscosity average molecular weight of about 94 000 in 85% formic acid at 20°C[14], and a crystallinity from density measurements[15] of 17%. This material was used extensively as salt uptake was able to be measured conveniently over a period of days. It was found by Karl Fischer analysis to contain 2.39 ± 0.06% water. The nylon-6,6 sample (ICI Maranyl A-100) was found to be of higher crystallinity (47%) and as expected[16] salt uptake was much slower. Its viscosity average molecular weight using Taylor's constants[17] (for 90% formic acid at 25°C) was approximately 18 000.

Analytical reagent grade anhydrous zinc chloride and lithium bromide (E. Merck and Co.) were used, with care taken to avoid premature moisture uptake. Solvents (water and methanol) were distilled before use.

Measurement of uptake

Kinetic studies. A variety of techniques were used to measure the penetration of salt solution into the polymer as a function of time.

Polymer cross-sections were examined with a Nikon SMZ zoom microscope equipped with automatic photographic facilities. For higher magnification carbon coated samples were inserted in a Jeol JSM U3 scanning electron microscope (SEM), and the area where salt had penetrated showed as a pale region, primarily due to atomic number effects upon contrast. Images were from secondary electrons emanating from a layer extending several microns below the surface. Extent of salt penetration across the specimen was thus possible by optical microscopy for systems exhibiting fast rates, and by SEM for slow rates or where exposure times were short.

The depth of penetration was also determined using an 'EDAX II' analyser. In the absence of 'line-scan' facilities (which allow the most convenient method for obtaining elemental abundances across a section of sample) incremental spot readings were obtained, as shown in *Figure 1*. It was found that by measuring 'counts' (for example, ZnKα X-rays of 8.63 KeV) for a given constant, small area, one could 'integrate' for a large number of consecutive regions, until a sudden reduction was observed. When equivalent areas were taken (a) to the interior of the penetration boundary where counts were minimal, (b) to the exterior and (c) centred about the boundary, one found that the average of the first two readings corresponded to the third. This result confirmed that the contrast effect obtained from the secondary electron image was generally an adequate measure of penetration.

Penetration was also measured using wavelength dispersive analysis (WDA). However, edge effects often occurred, limiting the accuracy of this method. Microscopic examination of the sample during microprobe analysis allowed correlation between surface contrast and 'zinc counts' to be made.

Measurement of concentration profiles

To distinguish between Case I, Case II and anomolous diffusion, concentration profiles were also required. These were obtained indirectly by EDA methods as described in the preceding section, as well as by WDA. In the former, only a 'histogram' was possible with available facilities, compared with the line scan achievable directly using WDA. (Many SEM's are now equipped with ancillary devices to enable EDA line scan data to be obtained routinely.) In these preliminary studies the more convenient time-scan method was employed instead of the point count technique. In addition, elemental 'X-ray maps' for a given area provide a qualitative indication of concentration, particularly if coating minimizing background (for example, carbon instead of gold) are employed.

Measurement of salt concentration

Although the absolute concentrations of salt in nylon were not required to determine the type of diffusion occurring, attempts were made using microprobe analysis and atomic absorption analysis as evidence exists for cracking activity being salt concentration dependent[9].

Quantitative microprobe analysis was undertaken for zinc by comparing levels found in the penetrated region with those found for a zinc metal standard under the same operating conditions. As high accuracy was not essential standards of known zinc contained in a polymeric matrix were deemed unnecessary.

For atomic absorption analyses, (thick) sections typi-

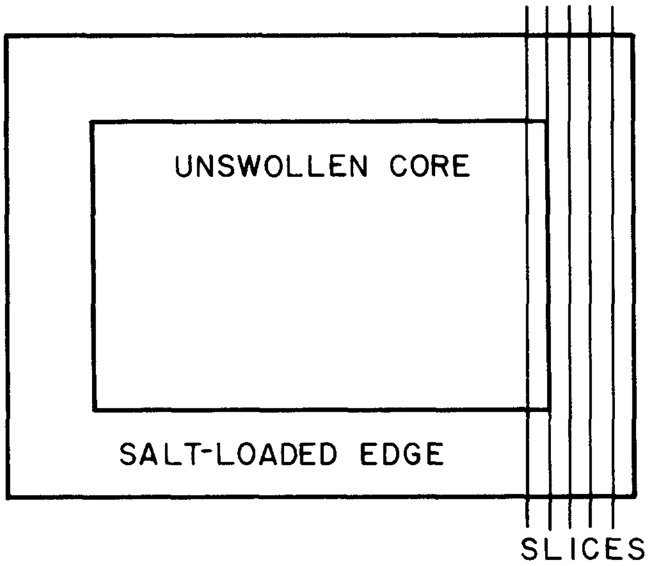

Figure 2 Preparation of slices of polymer for atomic absorption analysis

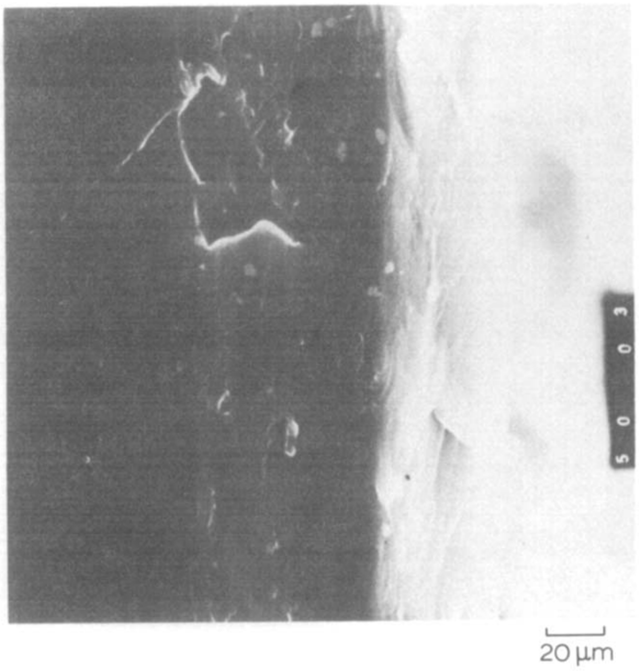

Figure 3 As received nylon-6 treated with 5M $ZnCl_2$ for 2.5 days. Magnification 620x

cally 30–40 μm thick were microtomed as shown in *Figure 2*, weighed using a micro-balance and dissolved in formic acid. Dilutions were made to a final concentration of 10% formic acid and analyses were made using zinc chloride standards, also in 10% formic acid. 'Matrix effects' which could arise from polymer being present were considered to be small, and levels of zinc which might be present in the untreated polymer (as processing additive or stabilizer) were also expected to be much less than absorbed salt. Zinc standards with added (untreated polymer) were prepared to measure these factors.

RESULTS AND DISCUSSION

As received nylon-6 with 5M $ZnCl_2$

Uptake of zinc chloride is readily observed by SEM. The right edge of a sample immersed for 2.5 days at 20°C is illustrated in *Figure 3*. Salt has penetrated from this edge and occurs as a pale featureless area. It is this area which is shown by EDA and WDA to be rich in zinc ions. The darker region to the left corresponds to the unaffected central core of polymer.

When samples are washed with water, an outer porous material is produced, *Figure 4* (from ref. 12). In this case, both the porous and light grey regions ('A' and 'B') at right are rich in zinc, as shown by the X-ray map (*Figure 5*, ref. 12), but dark region 'C' at left is essentially devoid of zinc. At high resolutions, X-ray analysis indicates that zinc chloride is higher in region B than A, because of the lower overall density of the porous zone, together with some leaching during sample preparation. All subsequent data are obtained from samples which have been dried but not washed.

Microprobe line-scans of 5M $ZnCl_2$ treated nylons (long immersion periods, 18 and 46 days), are shown in *Figures 6* and *7*. Edge effects are prominent in the first example, but when the resulting etched path is monitored by travelling microscope a corrected measure of salt penetration can be made. In both examples, the zinc concentration remains essentially unchanged with penet-

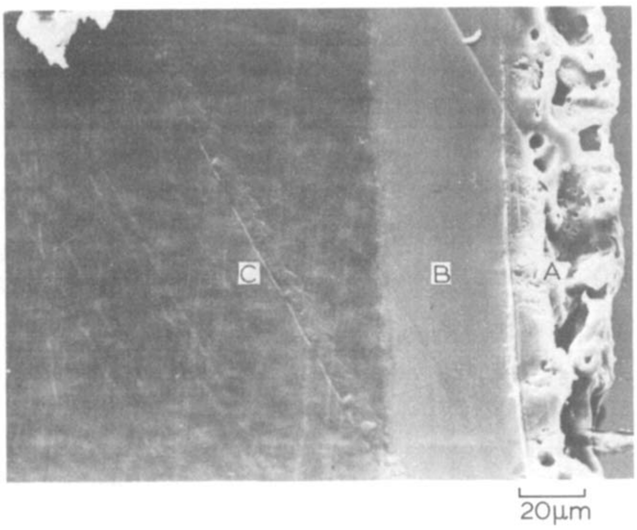

Figure 4 Cross-section of nylon-6 showing outer porous region (A), salt laden region (B) and unswollen core (C). Magnification 630× (Published by courtsey of *J. Mater. Sci.* (1979, **14**, 2881))

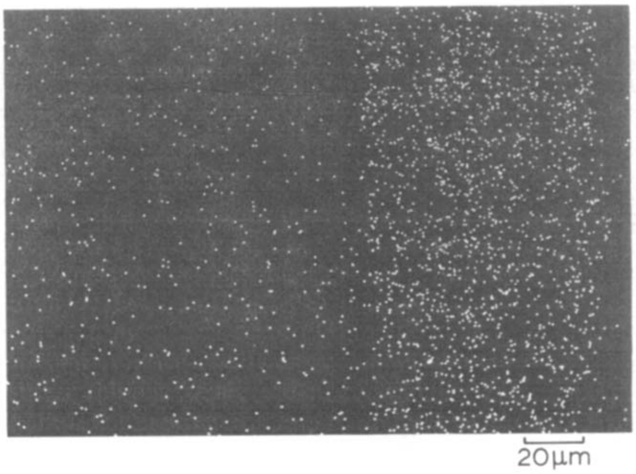

Figure 5 X-ray map corresponding to *Figure 4*, showing Zn distribution. Magnification 630× (Published by courtsey of *J. Mater. Sci.* (1979, **14**, 2881))

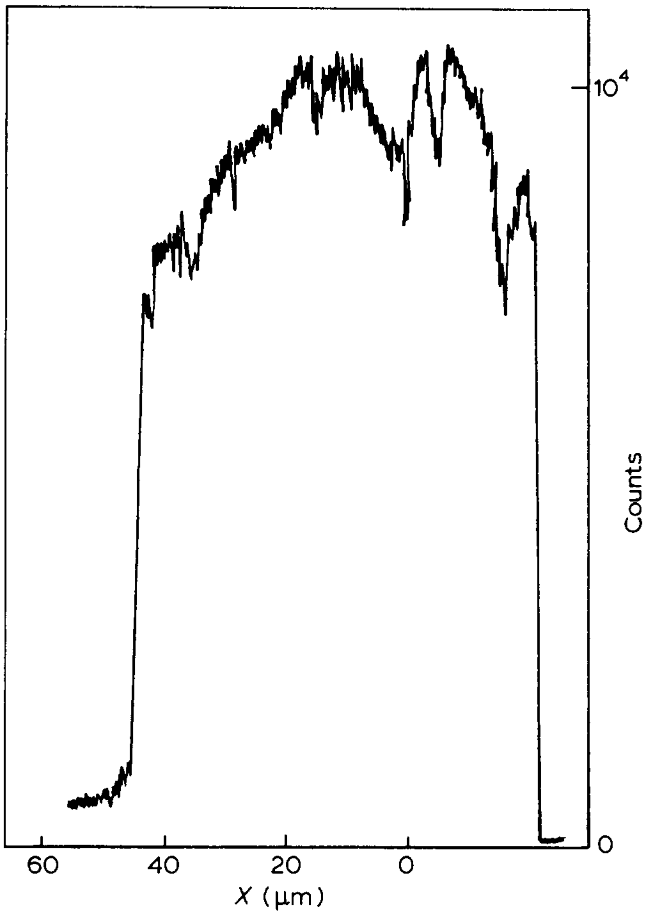

Figure 6 Nylon-6 treated for 18 days with 5M $ZnCl_2$; microprobe scan (specimen edge corresponds to right hand side of distribution)

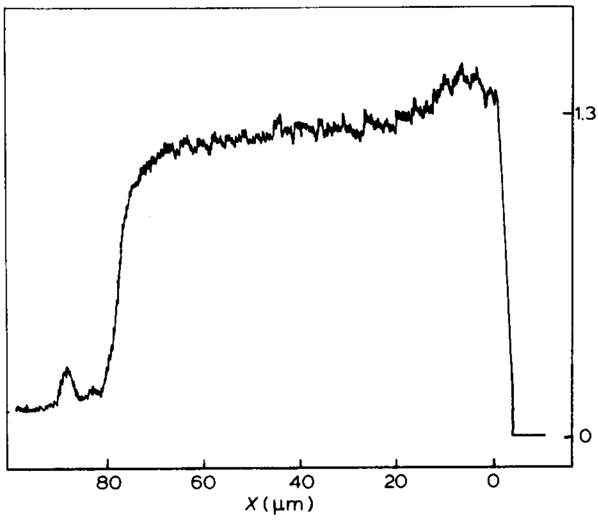

Figure 7 Nylon-6 treated for 46 days with 5M $ZnCl_2$; microprobe scan

ration distance, until the zinc-free boundary is reached. The dramatic reduction in zinc at the boundary is consistent with SEM data and EDA results. The profiles more closely resemble Case II transport than anomolous transport[6,7,18-21], with the Fickian region in front of the sorption discontinuity (*Figure 8*) being hard to resolve.

When penetration is plotted against time, a linear relationship holds but only at longer immersion times (*Figure 9*). The measurements at 2.5 and 5.0 days suggest that a Fickian relationship might be obeyed, but more 'short-exposure' data would be required to substantiate this. The progression for the 5M $ZnCl_2$/nylon-6 system is thus most likely to follow that shown in *Figure 10*, with initial Fickian behaviour at short exposure times, developing to essentially Case II transport at longer times (i.e. with miniscule Fickian region).

As received nylon-6 with 4M $ZnCl_2$

For these samples the line scan data suggests anomalous diffusion, with a more gradual fall of in zinc concentration being recorded at the boundary (*Figure 11*). However, preliminary kinetic data shown in *Figure 12* indicate a linear relationship between penetration distance and $t^{\frac{1}{2}}$, indicating that Fickian transport is important within the time-frame used.

Quantitative analysis of zinc in nylons

The following preliminary data serves to indicate the potential of the two methods. Levels of zinc found in

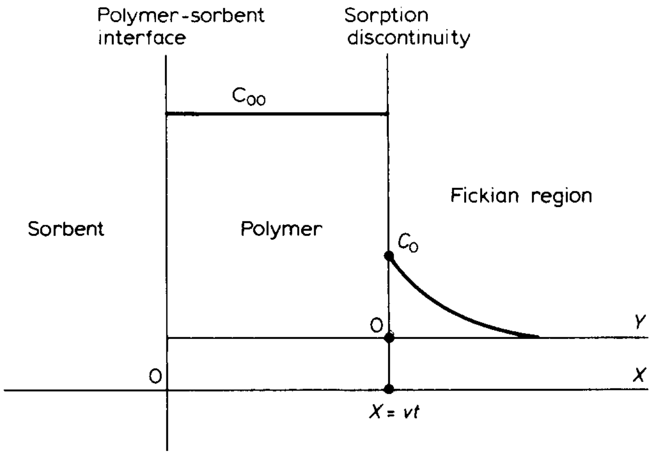

Figure 8 Anomalous diffusion according to Peterlin[18] (Published by coursey of Hüthig and Wepf Verlag, Basel; A. Peterlin *Makromol. Chem.* 1969, **124**, 136, Figure 1)

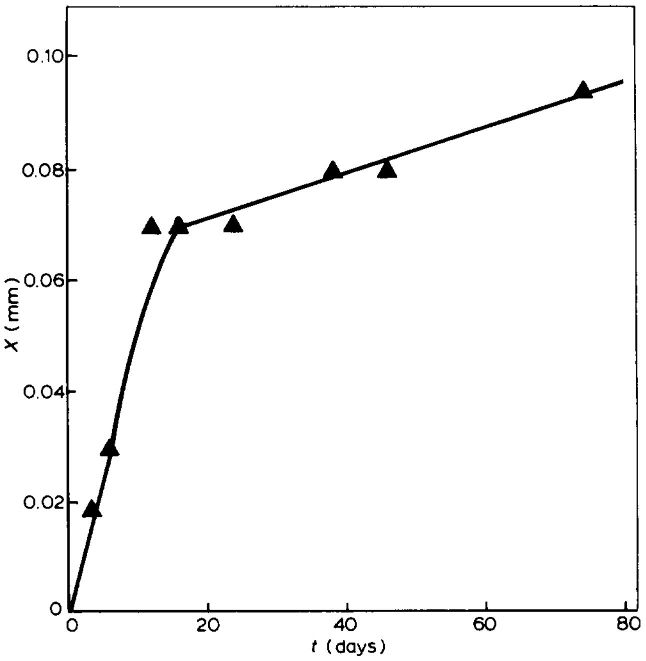

Figure 9 Uptake kinetics of 5M $ZnCl_2$ in nylon-6 showing Case II transport at longer immersion times

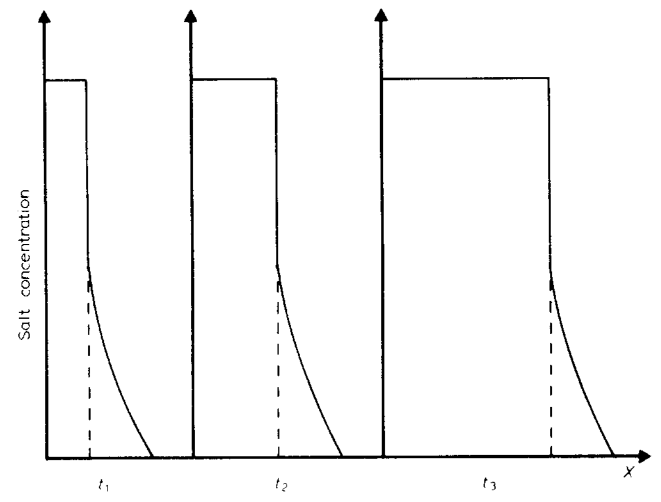

Figure 10 Schematic transport mode for 5M $ZnCl_2$ in nylon-6

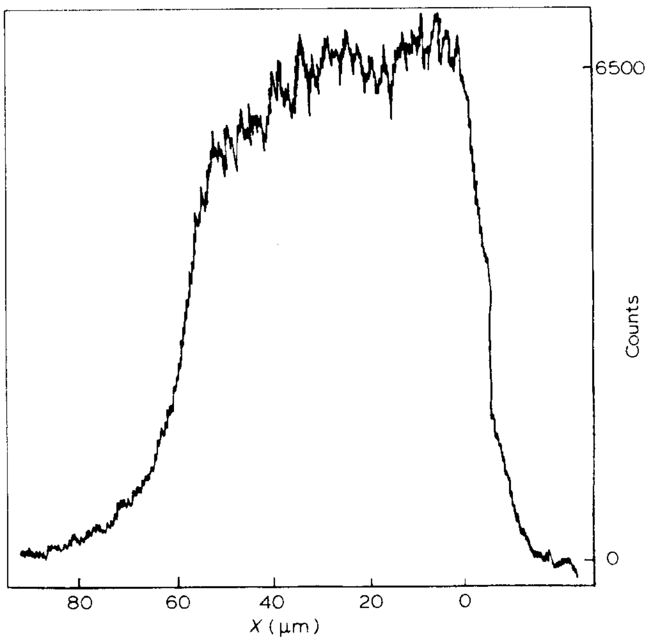

Figure 11 Microprobe zinc profile for 4M $ZnCl_2$ in nylon-6, immersed for 18 days

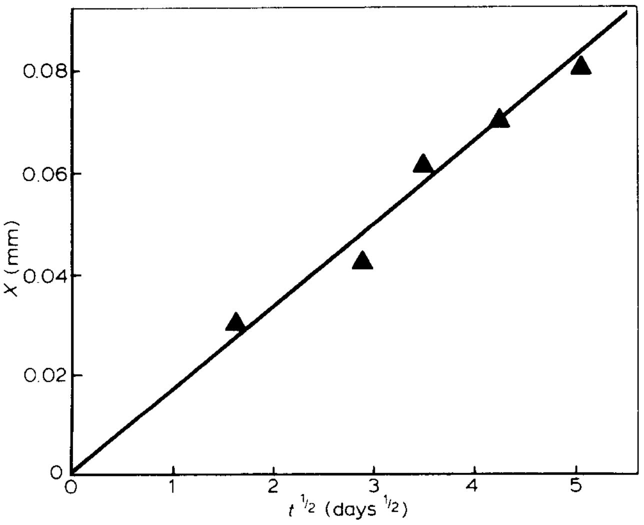

Figure 12 Fickian kinetics for 4M $ZnCl_2$ in nylon-6

nylon using WDA are given in *Table 1*, and show the expected increase with salt concentration.

Another section of the third sample (i.e. 46 day exposure) was then microtomed and the results obtained are given in *Table 2*. It can be seen that there is inadequate control of section thickness, so that no sensible concentration profile can be drawn. However, assuming the concentration remains constant from the outer edge to a depth of 0.023 mm the estimate of 10.2% agrees within experimental error. Major sources of error are expected to be thickness measurement of each slice, weight determination and salt contamination during sectioning. Using zinc standards with boty nylon absent and present, no significant difference was observed. The highest concentration of zinc recorded corresponds to a molar ratio of approximately one Zn to three carboxyl oxygens in the polymer chain.

Effect of polymer annealing

Samples of nylon heated to 130°C in paraffin oil for 2 h and then quenched were found to show different kinetic behaviour to the 'as received' polymer. A transition from Fickian to anomalous/Case II transport is suggested from the data given in *Figure 13*. The effect of thermal treatment has been to reduce the bulk moisture level from 2.4 to 1.1%, but it is also expected that changes in crystallinity, particularly at the surface, will also occur.

It should be noted, however, that the following trend seems to exist; at very high (5M) zinc concentrations with nylon containing moisture, or at lower (4M) zinc concentrations with dry nylon, show Case II diffusion occurs. Where lower (4M) zinc and wet nylon conditions exist, more rapid Case I uptake arises. However, further experiments where careful uptake measurements are performed, at short times, with nylons of known, independently varied moisture content and degree of crystallinity need to be undertaken to substantiate this hypothesis.

Effect of salt concentration and temperature

Transport behaviour is known to depend upon environment, temperature and penetrant activity[7,22]. When the distance of penetration after 25 days at 20°C was measured as a function of zinc chloride concentration, it was found that very low uptake occurred just below 4M

Table 1 Quantitative data by microprobe analysis

Penetrant concentration M	Immersion time (days)	Zinc in penetrated region (wt %)
4	18	6.6
5	18	9.7
5	46	12.8

Table 2 Results of atomic adsorption analysis of microtomed nylon-6

Distance from edge (mm)	Zinc content (wt %)
0.0 –0.023	10.2
0.023–0.131	4.9
0.131–0.173	0.3
1.173–0.217	0.5
0.217–0.283	0.3

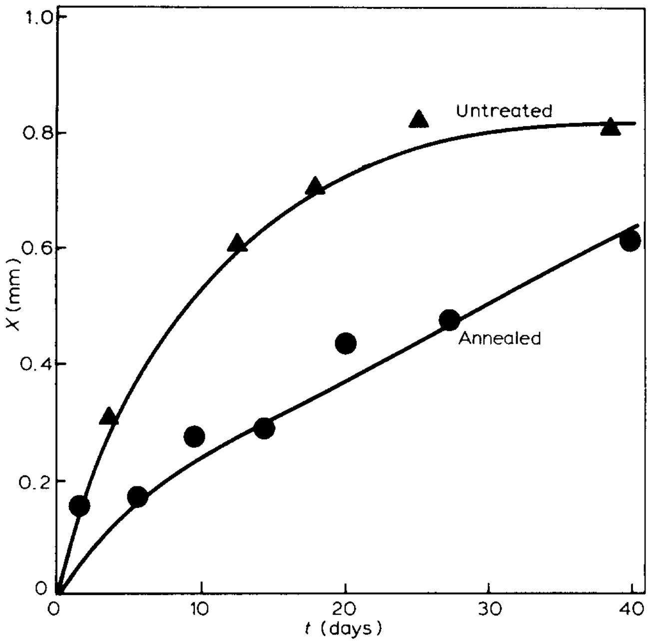

Figure 13 Kinetics of 4M $ZnCl_2$ in as received (▲) and annealed (●) nylon-6

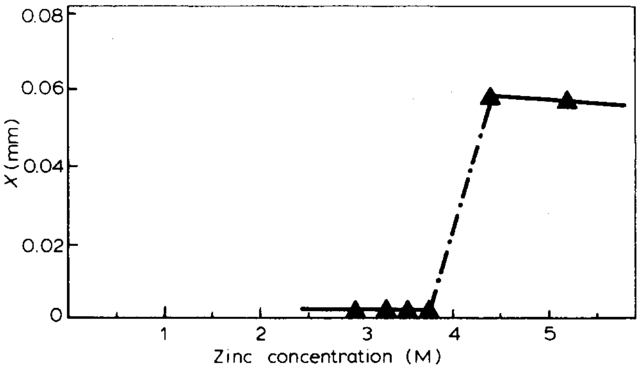

Figure 14 Distance of penetration in nylon-6 after 25 days, as a function of $ZnCl_2$ concentration

(*Figure 14*). There is no obvious stoichiometric reason for this trend, except that at concentrations exceeding 4M, halide ions will coordinate directly to the zinc cation. This lower solvation state will facilitate coordination directly with polymer carboxyl oxygen, in accordance with Dunn's evidence[9]. An alternative explanation, phrased in terms of solubility parameters is less able to correlate with the trend shown in *Figure 14*.

When both nylon-6 and -6,6 are immersed in 5M $ZnCl_2$ at 80° or 100°C (i.e. above the T_g), substantial swelling occurred within two hours and dissolution was complete within a day. At lower zinc chloride concentrations (3M), swelling was slower, but dissolution still occurred within two days at 80° and four days at 100°C. Unusually, nylon 66 was embrittled when immersed in 1M$ZnCl_2$ at 80° and 100°C. Surface crystallization and crusting occurred instead of swelling. The reasons for this behaviour are not clear.

Lithium bromide studies

It was found that (unlike zinc chloride) no clear microscopic evidence of salt uptake could be found when concentrated aqueous lithium bromide was used. Attempts at using 'staining agents' including silver nitrate solutions were unsuccessful at revealing the halide. This corresponds with the lack of residual lithium salts found on washed nylon fracture surfaces[12]. However, 5M methanolic lithium bromide solution induced swelling, and rapid uptake of this solution was able to be followed, after coating, both optically (*Figure 15*) and using the SEM (*Figure 16*). Artifacts, possibly caused by the escape of volatile solvent inside the vacuum chamber prior to coating can be observed transposed above the lighter, penetrated region on the right. No concentration profiles have been obtained for these samples, but early kinetic data shown in *Figure 17* suggests that a similar mechanism to that for 5M$ZnCl_2$ may be operating, particularly at long immersion times. The higher rates of

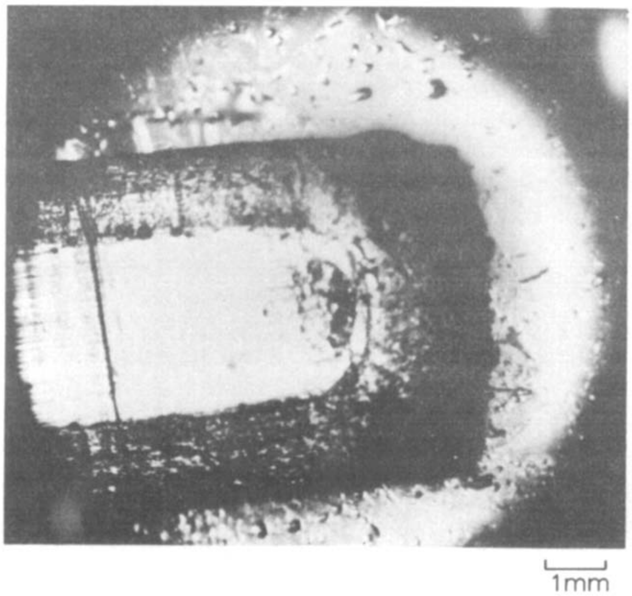

Figure 15 Cross-section of nylon-6, showing penetration of methanolic lithium bromide. Magnification 11x

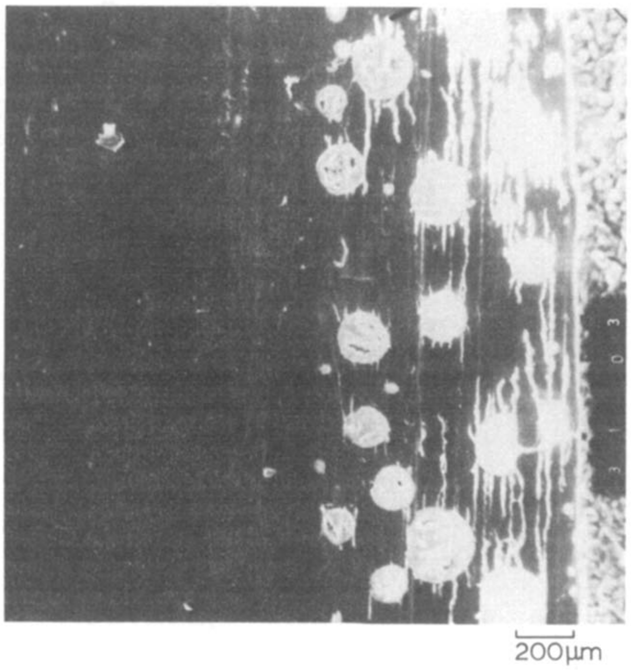

Figure 16 Scanning electron micrograph of methanolic LiBr penetrated nylon-6, showing artifacts. Magnification 60x

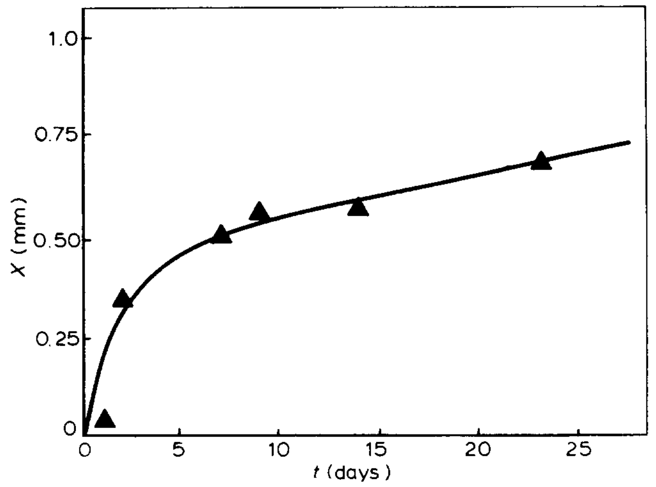

Figure 17 Kinetic data for 5M methanolic LiBr in nylon-6

uptake compared with aqueous zinc chloride solutions is consistent with differences in stress cracking activity[23] and may reflect the increased mobility of the lithium salt/solvent within the polymer matrix. Solvated lithium salts hydrogen bond to the nylon carboxyl oxygen via solvent molecules and are expected to be more labile than the Type 1 zinc salts[9].

CONCLUSIONS

In this study an attempt has been made to measure directly the diffusion of a penetrant into polymer, using X-ray analytical methods. Although there is ample scope for refinement of these procedures, it is concluded that SEM, EDA and WDA all offer several advantages over existing alternatives. Sample preparation is simple, and dimensional resolution can be high. The techniques described are particularly suited to the salt/nylon system, as the polymer becomes 'transparent' to the X-ray detector, making sensitivity and discrimination high. However, it is envisaged that by appropriate penetrant labelling methods, diffusion phenomena in other polymers, for example, additive migration in thermoplastics and elastomers, could be monitored.

Aqueous 5M $ZnCl_2$ solution appears to obey Fickian diffusion behaviour initially in nylon-6, but soon progresses to Case II transport, with little evidence for a Fickian region at the boundary. As salt concentration is lowered, the Fickian region is more pronounced, and anomalous diffusion is now evident. Below 4M, very little uptake in unstressed nylon-6 is detected at 20°C.

Methanolic lithium bromide (5M) appears to diffuse in a similar way to the zinc salt at the same concentration. However, data for this salt (particularly with water as solvent) was less readily obtained. By developing X-ray analysis procedures further, measurement of uptake at short exposure times, in samples with well-characterized moisture content and crystallinity should enable a mechanism for salt transport to be developed. The method may also allow uptake to be measured after short exposure to agents at elevated temperatures, enabling an activation energy to be calculated.

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