H→D exchange between poly(N-t-butyl acrylamide) and absorbed heavy water

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A spectroscopic technique for the study of the H→D exchange reaction between the functional groups of a polymer and absorbed heavy water is described and the results of an investigation of the exchange of the amide proton of poly(N-t-butyl acrylamide) reported. The incomplete exchange of the amide groups and the factors determining the rate of the exchange are discussed.

INTRODUCTION

Studies of the H → D exchange between the protons of the functional groups of polymeric materials and heavy water fall into two groups; those concerned with the exchange of polymers dissolved in excess heavy water and those concerned with the exchange of solid polymers containing absorbed heavy water. Both fields of study have been directed toward the elucidation of some aspect of polymer structure.

Many polymers possess hydrophilic functional groups and are capable of absorbing moderate quantities of water when exposed to water vapour or immersed in liquid water. When such polymers absorb heavy water, exchange can occur with the labile protons of the polymer. Such exchange has been studied in detail for the commercially important polymers nylon[1], silk[2], keratin[3] and cellulose[4]. The diffusion and swelling processes which occur simultaneously with the exchange reaction coupled with the complex chemical structure and partial crystallinity of the polymers studied, complicates the interpretation of the experimental data. In sharp contrast to the solution field[5], very little is known of the kinetics and mechanism of the exchange reaction itself between the labile protons of the functional groups and the absorbed water molecules. For these reasons the present investigation is concerned with the H → D exchange of poly(N-t-butyl acrylamide) which is non-crystalline and of known and relatively simple chemical structure. The first part of this paper describes the experimental technique adopted to monitor the exchange reaction.

EXPERIMENTAL

Preparation of poly(N-t-butyl acrylamide) films

Poly(N-t-butyl acrylamide) was prepared from the commercially available monomer by the method described by Klotz *et al.*[6] for the preparation of poly(isopropyl acrylamide). After repeated washings in distilled water the polymer was freeze dried from methanol for convenient storage. The intrinsic viscosity of the polymer in chloroform at 25°C was 0.096 dl/g. Clear flexible films of ~5 μm thickness were prepared by casting on a mercury surface from a solution of the polymer in spectroscopic grade chloroform.

Conditioning of polymer films

Polymer films were conditioned for periods in excess of three days by immersion in solutions of known pH at room temperature prior to use in any H → D exchange experiment. The conditioning solutions of pH between 1 and 3 were solutions of hydrochloric acid whilst those of pH between 11 and 13 were sodium hydroxide solutions. Conditioning solutions of intermediate pH were made up from commercial buffer tablets. Longer periods of conditioning were found not to affect the exchange kinetics and spectroscopic investigations did not reveal any deterioration of the polymer films (e.g. hydrolysis) even after several months.

Deuteration technique

The technique is essentially a modification of that described by King *et al.*[2] except that the polymer film is exposed to a flowing, rather than a static, vapour of heavy water.

The apparatus consists of a thermostatically controlled glass cell G (see *Figure 1*) sealed with calcium fluoride windows. Access to the cell is via three glass side arms fitted with ground glass joints. The polymer film F is mounted on a wire frame and attached to a ground glass stopper and enters the cell via one of the side arms. The two remaining side arms are attached to glass pieces to which are fitted a manometer, four traps and a vacuum pump as shown. Traps A and C contain degassed D_2O and traps B and D degassed H_2O. The temperature of the contents of each trap is controlled by immersion in a water jacket through which water is pumped from a thermostatically controlled bath. The flow of water from the baths is indicated by arrows in *Figure 1*. Traps A and B are maintained at 1°C above the temperature of traps C and D, the actual temperatures being determined by the vapour pressure of water vapour required. The cell G is also thermostatically controlled but at a constant temperature of 25°C. After evacuation of the apparatus to remove all air, a flow of either D_2O or H_2O vapour across the faces of the polymer film can be established by opening traps A and C or B and D, respectively. The entire apparatus was permanently mounted with the cell in the sample beam of a Grubb Parsons Spectromajor infra-red spectrometer and the whole enclosed in a polyethylene hood
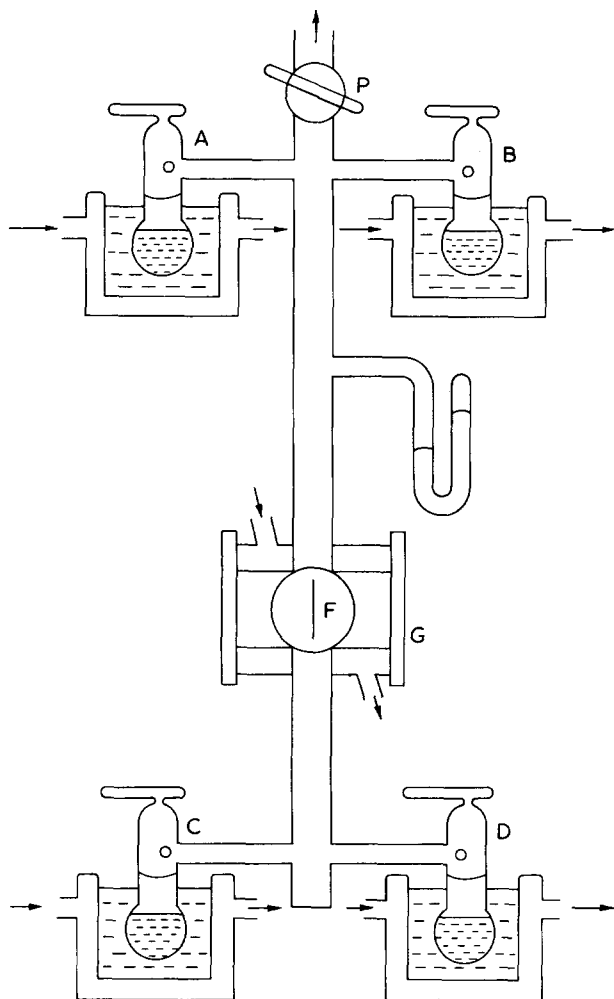
Figure 1 Apparatus for H → D exchange of polymer films

thermostatically controlled at 27°C to prevent condensation on the inside of the glassware.

To perform a normal H → D exchange experiment, a sample of polymer film was removed from the conditioning solution and blotted dry with filter paper before being attached to the wire frame with adhesive and fitted into the cell G. Evacuation for 15 min (10^{-3} mmHg) removed all the air from the apparatus and the water from the polymer film. After isolation of the apparatus from the vacuum pump by closing tap P, the infra-red spectrum of the sample was recorded from 4000–1000 cm^{-1}. To prevent the temperature of the film rising above 25°C during the exchange, the beam of the spectrometer was blocked off by placing a card in front of the cell. A flow of D_2O vapour of predetermined vapour pressure (relative humidity) was established by opening traps A and C which were suitably thermostatically controlled. At intervals the absorbance of the N–H peak at 3310 cm^{-1} was determined by removal of the card for a few seconds. This procedure is referred to as 'chopping' in the remainder of this text. At the end of the exchange experiment the apparatus was evacuated and the spectrum recorded.

The results are expressed in the form of a plot of the percentage reduction of the N–H absorbance against time. If the Beer–Lambert law holds for the amide absorption, then the percentage reduction of the N–H absorbance is equal to the percentage exchange of the amide groups. The validity of the Beer–Lambert law has not been checked but

might be expected to hold for a non-crystalline polymer of the type employed in this investigation. Validity of the Beer–Lambert law is not a requirement of the arguments put forward to explain the experimental data presented here.

Absorption rate and isotherm determinations

The rate of absorption of heavy water vapour and the absorption isotherm for poly(N-t-butyl acrylamide) were each determined gravimetrically using a sensitive quartz helical spring. Details of the method can be found elsewhere[2]. When expressed on a mole basis identical results were obtained for H_2O and D_2O absorption.

H → D exchange of N,n-butyl acetamide/heavy water mixtures

The method used by Feidelseit[7] for determining the rate constant for the H → D exchange of N,n-butyl acetamide dissolved in excess heavy water (1 M solution of amide) was adopted. Quantities of the amide and suitably buffered heavy water were syringed into a small glass vessel and shaken together before transfer to a 1 cm thermostatically controlled cell mounted in a Grubb Parsons Spectromajor with which the exchange could be monitored from the increase in the OH absorbance at 6830 cm^{-1}. The experimental data gave an acceptable fit to the semilogarithmic plot for a second order reaction in which the forward and back reaction have the same rate constant, i.e.

$$-CONH- + D_2O \underset{k}{\overset{k}{\rightleftharpoons}} -CONH- + HDO$$
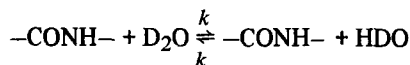
A more refined analysis was not felt justified in view of the accuracy of the experimental data and the interpretation to be put upon the results. Experiments were performed at two concentrations, 2.30 g amide +0.24 g heavy water corresponding to 0.6 mol D_2O per amide group and 2.30 g amide +0.12 g heavy water corresponding to 0.3 mol D_2O per amide group. The pH of the reaction mixture was determined after the exchange reaction was completed using a commercial meter with a glass electrode.
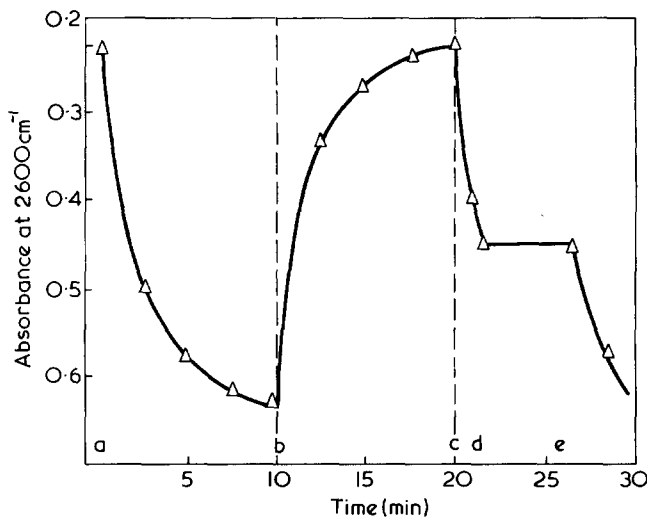

Figure 2 Absorbance at 2600 cm^{-1} measured by chopping technique. Initially polymer in equilibrium with H_2O vapour at 88% r.h. At time (a) H_2O flow replaced by D_2O flow. At time (b) D_2O flow replaced by H_2O flow. At time (c) H_2O flow replaced by D_2O. At time (d) flow stopped. At time (e) flow restarted
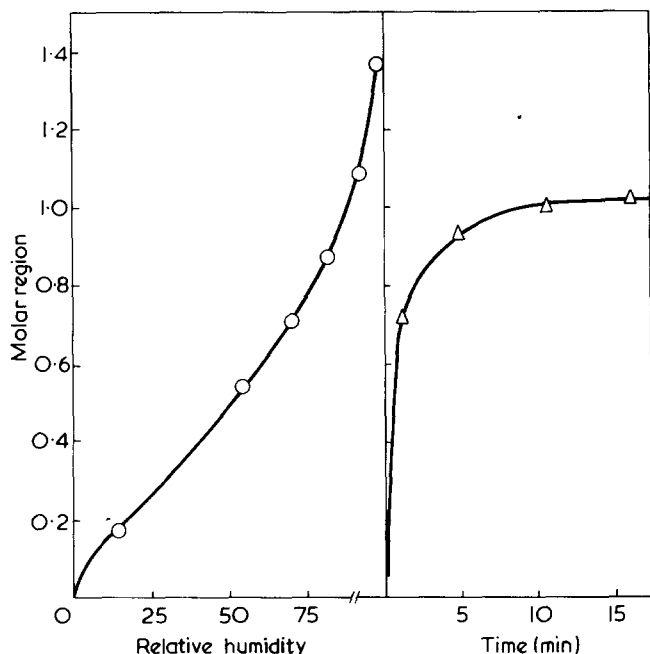
Figure 3   Isotherm and uptake curve for poly(*N*-t-butyl acrylamide) at 25°C. Molar region: moles water per mole amide group of polymer. Uptake curve determined at 88% r.h.

RESULTS AND DISCUSSION

Deuteration technique

When a polymeric material is immersed in heavy water or suspended in heavy water vapour, the heavy water vapour molecules diffuse into the polymer matrix. The time for the system to reach equilibrium depends upon the diffusion coefficient of the heavy water in the polymer and the geometry of the polymer sample. The exchange reaction between the polymer functional groups and the absorbed heavy water begins immediately, and only if the diffusion is rapid does the exchange reaction itself determine the rate of H → D exchange. As the exchange proceeds HDO and even H_2O build up inside the sample and self-diffusion of these species out of the sample and of D_2O into the sample becomes important*.

The observed rate of H → D exchange will therefore be a complex function of the various diffusion coefficients (each concentration dependent), the geometry of the polymer sample, the equilibrium heavy water concentration within the polymer and the rate constant of the exchange reaction itself. Even if an expression for the observed rate of exchange could be derived in terms of these quantities the necessary diffusion data are not available to allow the rate constant to be extracted.

In the present work the exchange has been monitored spectroscopically using the N—H hydrogen bonded stretching mode at 3310 cm^{-1}. In this way it is possible to use polymer films of ~5 μm thickness, reducing the time for the sample to come to equilibrium with heavy water vapour to a minimum. *Figure 3* shows that films of poly(*N*-t-butyl acrylamide) of suitable thickness come effectively to equilibrium with heavy water vapour in 5 min.

As the exchange reaction proceeds HDO builds up inside the film and the back reaction D → H becomes in-

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* Replacement of HDO and H_2O by D_2O within the polymer may well occur by proton transfer rather than self-diffusion of the molecular species, but this does not affect the argument here.

creasingly important. This not only complicates the analysis of the exchange data but prevents the monitoring of the exchange by observation of the absorbance of the N—H peak, since a broad OH band is superimposed upon it. Consequently in earlier related studies[1-4] in which the exchange of a polymer has been monitored spectroscopically, it has always been found necessary to remove the HDO from the sample by evacuation prior to making an absorbance measurement. This complication prevents the continuous monitoring of the exchange process and makes kinetic investigations difficult. The necessity for this evacuation has been avoided by a modification of the normal experimental procedure.

The build up of HDO within the polymer film has been found to be a result not of slow diffusion of HDO within the polymer film, but to the build up of a static vapour layer at the surface of the film rich in HDO. By arranging for a flow of D_2O vapour across the faces of the film, the build up of HDO can be prevented and the exchange of the N—H proton can be monitored directly from its absorbance at 3310 cm^{-1} whilst the polymer contains absorbed heavy water. Provided the exchange reaction has a half-life greater than about 10 min, the exchange reaction and not the diffusion processes becomes the rate determining step over the observed rate of exchange. As a result of the flow, build up of HDO within the film is prevented and the polymer possesses essentially pure D_2O throughout the entire course of the exchange. In essence the reacting system is that of polymer plus absorbed D_2O at a constant concentration, and the reaction might therefore be expected to be pseudo first order with respect to the concentration of the N—H groups of the polymer, the exchange proceeding to completion.

The rapid replacement of HDO by D_2O within the film by the maintenance of a flow of D_2O vapour across the faces of the polymer film can be demonstrated most easily by use of a film of poly(*N*-t-butyl acrylamide) conditioned at an alkaline pH, so that exchange of the N—H group of the polymer is effectively prevented (see later). If such a film is mounted in the apparatus and evacuated for 15 min and then exposed to a flow of H_2O vapour by opening traps B and D, a broad OH absorption appears under the polymer N—H absorption at 3310 cm^{-1}. If the spectrometer is now set at 2600 cm^{-1} (a region in which the polymer with absorbed H_2O does not absorb) and the flow of H_2O replaced by one of D_2O (simply by closing traps B and D and opening traps A and C) a rapid increase in the absorbance can be monitored by the chopping technique, showing the replacement within the polymer of H_2O by D_2O which absorbs in this region. Replacement is 90% complete within 5 min. If the D_2O flow is now replaced by an H_2O flow an equally rapid fall in the 2600 cm^{-1} absorption results from the replacement of D_2O by H_2O within the film. Should the flow of either H_2O or D_2O be stopped by closing one trap only so that the film is exposed to a static vapour, replacement ceases immediately. Reopening the trap to reinstate the flow results in a continuation of the replacement process (*Figure 2*).

In any exchange experiment the absence of HDO in the film can always be confirmed by chopping at 3500 cm^{-1}, a region where absorbed HDO absorbs strongly, but just outside the polymer N—H absorption.

H → D exchange of poly (N-t-butyl acrylamide)

Poly(*N*-t-butyl acrylamide) (PTBA) was chosen for study as it is structurally similar to poly(isopropyl acrylamide)
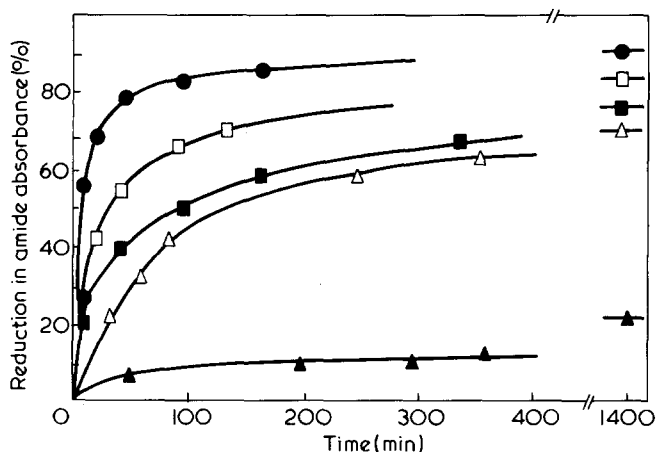
Figure 4 H → D exchange of conditioned films of PTBA at 88% r.h. (Internal concentration: 1.1 mole D_2O per mole amide group of polymer.) Conditioning treatments: ●, 0.1 M HCl; □, 0.01 M HCl; ■, 0.001 M HCl; △, buffer pH 4; ▲, 0.01 M NaOH
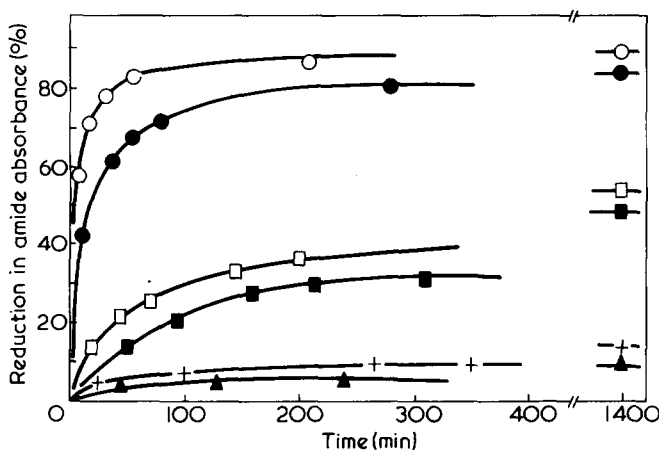

Figure 5 H → D exchange of conditioned films of PTBA at 66% r.h. (Internal concentration: 0.65 moles D_2O per mole amide group of polymer.) Conditioning treatments: ○, 1 M HCl; ●, 0.1 M HCl; □, 0.01 M HCl; ■, 0.001 M HCl; +, buffer pH 7; ▲, 0.01 M NaOH

(PIPA) a polymer for which extensive exchange data in solution is available[6]. PIPA is soluble in aqueous solutions and therefore unsuitable for the present investigation whereas PTBA is insoluble although capable of absorbing moderate quantities of water (see isotherm *Figure 3*). Films of PTBA can therefore be conditioned in buffered solutions prior to kinetic investigation. *Figures 4–6* show the exchange data for conditioned film of PTBA containing different concentrations of heavy water. Several important features relating to the exchange are evident from this kinetic data.

(a) Exchange occurs at a measurable rate for films conditioned between pH 2 to 7. Below this pH exchange is very rapid and governed by the rate of uptake of D_2O vapour by the polymer. Above pH 7 the exchange is very slow.

(b) Except for films conditioned at a pH less than 2, the rate of exchange, although initially rapid, decreases greatly as the exchange proceeds. As a result, the exchange effectively 'cuts off' at some extent of exchange dependent upon the conditioning pH and internal heavy water concentration. For convenience the phenomenon will be referred to as a 'cut off' in the remainder of the text.

(c) The higher the conditioning pH and the lower the

internal D_2O concentration, the lower the extent of exchange at the 'cut off'.

These results are in sharp contrast to those for the exchange of PIPA in solution[6] for which the exchange is acid and base catalysed with the rate constant for the base catalysed reaction much greater than that for the acid; the exchange going to completion. The solubility of PIPA prevents conditioning of films of the polymer. However, experiments on unconditioned films indicate similar behaviour. Films of PIPA cast from spectroscopic grade methanol solution exchange very slowly showing a distinct 'cut off'. If a film is cast from methanol containing traces of hydrochloric acid, then the resultant film exchanges rapidly initially, the rate increasing with the quantity of hydrogen chloride involved. If such a film is exposed to ammonia vapour to neutralize the acid prior to an exchange experiment, then the resultant film exchanges very slowly. These experiments would indicate that PTBA is not anomalous.

The pH at which a film is conditioned prior to an exchange experiment, greatly affects the kinetics of the exchange. This is believed to result from the hydrogen and hydroxide ions which enter the polymer along with other ions during the conditioning process and which remain in the film during the subsequent deuteration experiment and govern the rate of the H → D exchange reaction. The presence of such ions within the film after conditioning has been confirmed by desorption into distilled water from blotted conditioned films. No evidence of any conformational difference between films conditioned at different pH is apparent from the infra-red spectra of the films.

One possibility for the occurrence of the 'cut off' is that the hydrochloric acid present in the film as a result of the conditioning process slowly desorbs from the film during the deuteration experiment; the 'cut off' signifying the complete removal of the catalysing hydrogen ions. This however can be disproved in the following way. If H_2O flows for several hours across a film followed by a flow of D_2O, the resulting exchange–time plot is identical to that obtained from a similar film exposed to a D_2O flow immediately after the initial evacuation procedure. If the hydrochloric acid were desorbing from the film, it would do so during the H_2O flow, and little H → D exchange of the polymer would be anticipated on changing to a D_2O flow.

Before an exchange experiment the apparatus is evacuated to remove air which would hinder the flow of D_2O and
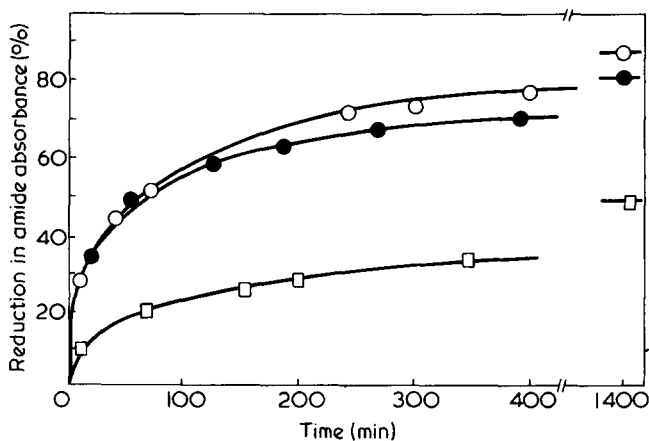

Figure 6 H → D exchange of conditioned films of PTBA at 35% r.h. (Internal concentration: 0.33 mole D_2O per mole amide group of polymer.) Conditioning treatments: ○, 1 M HCl; ●, 0.1 M HCl; □, 0.01 M HCl

greatly increase the time required for the film to reach equilibrium with the D_2O vapour[8]. This process also results in the complete drying out of the polymer film and concentrates the absorbed ions within the film. The pumping dry of the film can be avoided by very slowly evacuating the apparatus with one of the water traps open. In this way the air is flushed from the apparatus but the vapour pressure of water never falls much below that of the saturation vapour pressure of the water in the open trap, and the polymer retains its absorbed water. If the apparatus is eventually isolated and the H_2O replaced by a D_2O flow, the H → D exchange—time curve is identical to that of a similar film evacuated in the normal manner. Evacuating the film to dryness does not therefore alter the H → D exchange kinetics of the polymer—heavy water system.

Two features of the H → D exchange of PTBA require theoretical interpretation. One is the acid catalysed but not base catalysed nature of the exchange reaction and the other the appearance of the 'cut off' in the exchange.

The generally accepted mechanism[6] for the exchange of the amide group proton of polymers such as PIPA dissolved in excess heavy water involves N protonation for the acid catalysed mechanism and N proton extraction for the base catalysed mechanism.
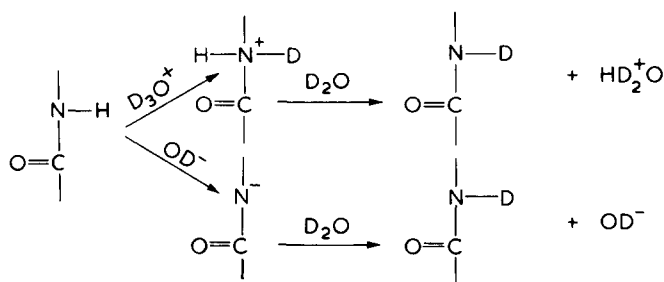
In solution, the intermediate ions are possibly both stabilized by hydration. In the polymer—absorbed water system far less water is available for hydration and this might well result in a dramatic reduction in the rate of the base catalysed reaction. There is evidence to suggest that the cationic intermediate of the acid catalysed mechanism does not require hydration. The species $-\text{CONH}_2-$ has been observed by Cannon[9] in chloroform and carbon tetrachloride solutions of amides and hydrogen chloride. In fact this species can be detected spectroscopically if a film of PTBA is exposed to the vapour above concentrated hydrochloric acid. No evidence is available to suggest that the anionic intermediate is stable without hydration.

Perhaps the most surprising aspect of the results is the appearance of the 'cut-off'. The maintenance through the flow technique of essentially pure D_2O within the polymer structure should lead to the complete exchange of all the polymer functional groups in a homogeneous polymer—heavy water system. Similar incomplete exchange observed with other polymers such as nylon[1], silk[2], keratin[3] and cellulose[4] has been attributed to the partial crystalline nature of these polymers, the crystalline regions being resistant to exchange. All the evidence suggests that PTBA is non-crystalline[10]. The variable level of the 'cut off' is also inconsistent with the assignment of the non-exchangeable amide protons to the crystalline regions of the polymer structure. King et al.[11] have produced evidence that the extent of exchange of the amorphous regions of the partially crystalline polymer, keratin, does decrease with the absorbed heavy water concentration in a similar manner to that noted here for PTBA.

It would appear that although PTBA is non-crystalline, the PTBA—heavy water system cannot be regarded as a homogeneous system. This inhomogeneity could well arise from the restricted molecular motion of the polymeric molecules in the solid polymer so that the amide groups of the polymer exist in a variety of molecular environments. In such a system the exchange of functional groups in the less favourable regions would only be expected to occur at high heavy water concentrations and acidic conditions. This situation does not arise in dilute solutions of polymers such as PIPA, because the increased molecular freedom of the polymer molecules leads to each amide group having a 'time-averaged' identical environment, so that the exchange follows simple pseudo first order kinetics with the exchange going to completion.

The explanations put forward for the 'cut off' and lack of base catalysis in the H → D exchange of PTBA are based upon the hypotheses that a lower rate of exchange is to be expected in regions of the polymer of low heavy water and hydroxonium ion concentration and that the base catalysed exchange mechanism is reduced in effectiveness due to the lack of heavy water available for hydration purposes. Some evidence in support of these contentions has been obtained. N,n-butyl acetamide is a liquid completely miscible with water and is representative of the repeat chemical structure of PTBA. (Other amides which are structurally closer to the repeat unit of PTBA are solids at room temperature.) The exchange of a 1 M solution of N,n-butyl acetamide in heavy water has been studied by Feidelseit[7]. At this concentration the rate constant for the exchange reaction, when plotted against pD, shows the typical parabolic shape with a minimum at a pD of 5.55. Adopting Feidelseit's experimental technique, the exchange of this amide has been studied at two concentrations corresponding to the concentrations employed for the PTBA studies. The results are shown in *Figure 7* and it can be seen that the minimum exchange rate has moved to a pD of 6.95 and 7.30 as the heavy water concentration was decreased. This result is consistent with the base rate constant decreasing more rapidly than the acid rate constant as the heavy water concentration is reduced.

If, as suggested here, the polymer—heavy water system is not homogeneous and the amide groups reside in a variety of molecular environments, then the molecular environment of a particular group would appear capable of changing during the swelling process which occurs during the absorption and desorption of water by the polymer. This is demonstrated in *Figure 8* in which the exchange of a film conditioned at a pH of 3 and deuterated in the normal manner is shown. The reaction shows the normal 'cut off' at about 60% exchange. If, after the exchange has effectively ceased, the polymer is evacuated to dryness for 15 min and then the flow of heavy water is restarted, the polymer undergoes a further small exchange. This process can be repeated several times with a decreasing amount of exchange occurring on each occasion. It would appear that amide groups that were initially in region of the polymer unfavourable for exchange have become redistributed in regions favourable to exchange during the desorption—absorption cycle. A similar explanation has been put forward to account for the fact that the deuteration of keratin and silk with heavy water vapour followed by evacuation and rehydrogenation with water vapour does not lead to complete rehydrogenation[2].

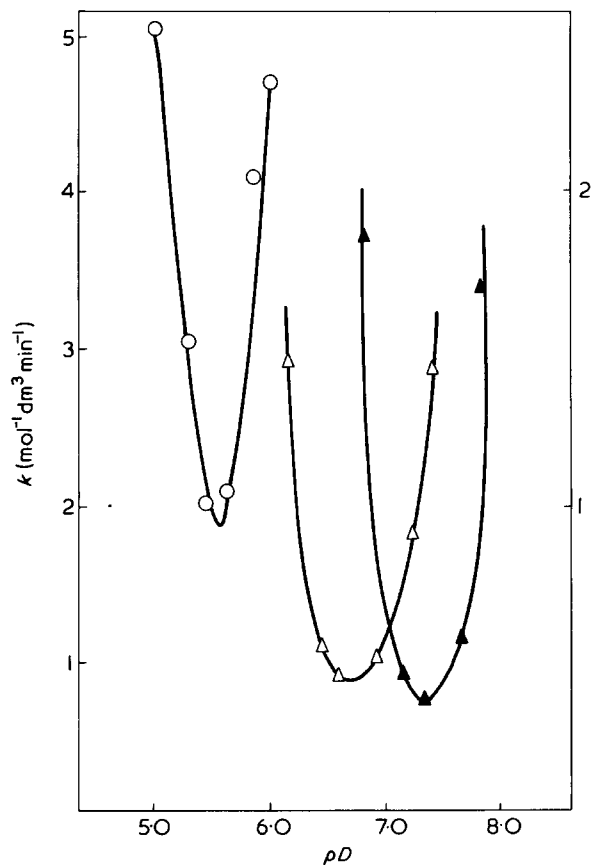The infra-red spectra of PTBA (and PIPA) films (*Figure 9*) show absorption maxima at 3430 and 3310 cm^{-1} cor-

Figure 7 Rate constant for H → D exchange of *N*,n-butyl aceta-
mide. ○ (left hand scale), 1 M amide 50 M D₂O recalculated from
results of Feidelseit; △ (right hand scale), 6.4 M amide, 4.3 M D₂O;
▲ (right hand scale), 6.66 M amide, 2.21 M D₂O

Figure 8 H → D exchange of PTBA film conditioned in 0.001 M
at 88% r.h. At time (a) sample evacuated to remove absorbed
heavy water for 15 min and flow of heavy water then re-established

Figure 9 Infra-red spectrum of PTBA. ——, Hydrogen form;
— — — —, partly deuterated polymer

responding to free and hydrogen bonded N–H groups.
Irrespective of the conditioning pH and of the absorbed
D₂O concentration the free and bonded groups have been
found to exchange at the same rate. This is also the case
for PIPA dissolved in heavy water. It is difficult to recon-
cile this observation with the hypothesis of inhomogeneity
of the polymer–absorbed heavy water system. The free
N–H groups would be expected to reside in isolation, buried
in the more hydrophobic regions of the polymer structure
and of low local heavy water concentration. Each of the
hydrogen bonded N–H groups must be adjacent to at least
one other amide group to which it is hydrogen bonded and
therefore generally in a more hydrophilic environment with
a higher local concentration of absorbed heavy water and
therefore presumably more likely to exchange.

Further experimental data of the exchange reaction,
particularly of other polymers and perhaps other sorbates
would appear essential before confident interpretation of
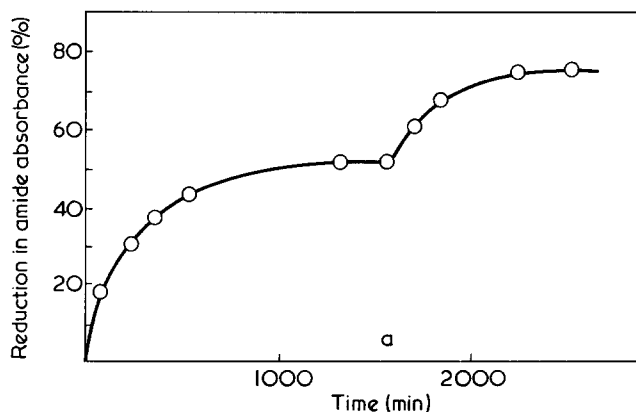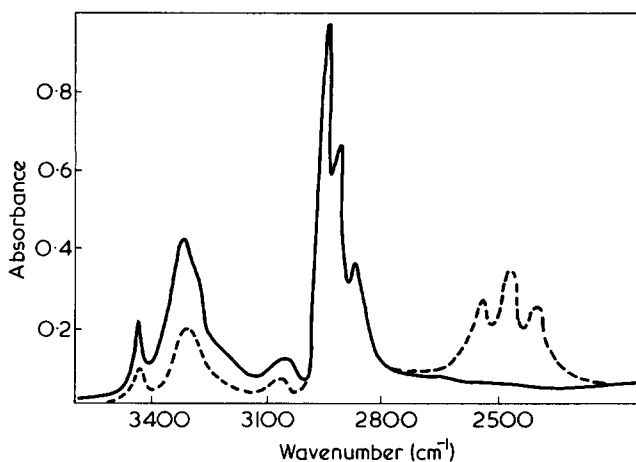the results reported here can be made.

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