*FT*i.r. and potentiometric study of basic polymer behaviour in the free form, in different bulks, in both solid state and aqueous solution

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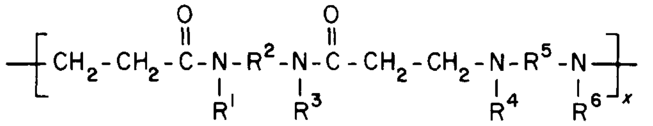
The behaviour of the polymer N_2LL having a poly(amidoamine) structure [obtained by polyaddition of *N,N'*-dimethyl-1,4-diaminobutane to 1,4-bis(acryloyl)piperazine], was studied by Fourier transform infrared spectroscopy and potentiometric techniques in the free form, blended, surface grafted and in a network with polyurethane. The different strengths of interaction via hydrogen bond of the N_2LL chain were evaluated in the different bulks, which showed that the polymeric chains have similar behaviour when in the linear form and anchored at one end to the surface of the polyurethane support, or when both ends are fastened. The different hydrophilic character of the N_2LL polymer and polyurethane chains is responsible for differences in behaviour in the solid state and in aqueous solution.

(Keywords: hydrophobic–hydrophilic polymer interaction; blend; networks; *FT*i.r. spectroscopy; potentiometric and permeability measurements)

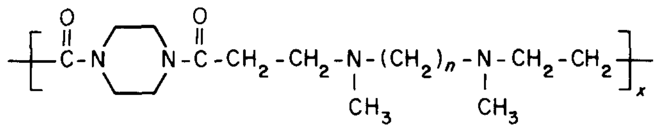
INTRODUCTION

It is well known that, due to cooperative effects between different repeating units, the behaviour of polyelectrolytes in protonation and complex formation must be described via 'apparent' thermodynamic functions that usually depend on the degree of protonation of the macromolecule[1]. A few years ago, however, it was found that some regular water soluble polymers, having a poly(amidoamine) structure (see below) show unusual behaviour: their monomeric units behave independently in protonation and complex formation[2]. Consequently, the behaviour of these polymers is similar to that of small molecules, for which the precise site of protonation and 'sharp' thermodynamic functions may be determined.



$$\left[CH_2-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{R^1}{N}-R^2-\underset{R^3}{N}-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_2-\underset{R^4}{N}-R^5-\underset{R^6}{N}\right]_x$$

Resins with a poly(amido amine) structure have been synthesized and the basicity constants determined by potentiometric techniques[3]. To study the behaviour of a particular N_2LL poly(amido amine) [obtained by polyaddition of *N,N'*-dimethyl-1,4-diaminobutane to 1,4-bis(acryloyl)piperazine] in different bulks, films of N_2LL blended with polyurethane, films of N_2LL surface grafted polyurethane and films of the material PUPA in which N_2LL is anchored to the polyurethane chains via its terminal groups[4] were synthesized and studied by Fourier transform infrared (*FT*i.r.) and potentiometric techniques. The arrangement and the behaviour of the polymer chains in these samples was investigated and compared with those of the free N_2LL polymer in solution[2] or in the crosslinked form[3].



$n = 4$ N_2LL

Knowing the frame of the polymer chains in the different bulks is useful in characterizing these materials of biomedical potential[4]. Some insights can also be gained into the binding of the protons and their distribution inside the polymer. The presence of electrical charges is in fact an important additional feature determining the suitability of materials for artificial implants. The N_2LL polymer interacts strongly with heparin even if mixed with other polymeric materials[5]. Hence a complete characterization of these polymers is necessary if we are to know how the charge is affected by factors such as pH and ionic strength[6].

EXPERIMENTAL

Materials

N_2LL polymer. The N_2LL polymer was synthesized as previously described[7]. The hydrochloride N_2LL was prepared by dissolving the N_2LL in a minimum amount of methanol and adding a 37% HCl solution dropwise under stirring to pH = 2; the polymer was then precipitated with ether and dried under vacuum (400 mbar*).

Polyurethane (PU) films. Films of PU were obtained by casting a 10% solution of Pellethane®$_{2363-80AE}$ in *N,N*-dimethylformamide (DMF) on a glass plate, followed by evaporation of the solvent under vacuum (400 mbar) at 70°C.

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* 1 mbar = 10^{-1} kPa

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Films of hexamethylenediisocyanate (HMDI) surface grafted PU and N_2LL surface grafted PU. Films of HMDI and N_2LL surface grafted PU were obtained as previously described[8].

Films of PUPA material. Films of PUPA material were prepared as previously described[4] by crosslinking the N_2LL poly(amidoamine) to the commercial PU via hexamethylenediisocyanate. Different samples of PUPA with different amounts of PU in the starting mixture were prepared: PUPA I (PU 1.0 g, N_2LL 0.4 g, HMDI 0.21 ml), PUPA I bis (PU 2.0 g, N_2LL 0.4 g, HMDI 0.21 ml), PUPA I penta (PU 5.0 g, N_2LL 0.4 g, HMDI 0.21 ml).

Films of crosslinked PU. The material with PU chains interlinked via hexamethylenediisocyanate (HMDI) was prepared by adding 10 g of a 10% solution of PU in *N*,*N*-dimethylformamide (DMF) to 10 ml of methylene chloride solution containing 0.21 ml of HMDI under a nitrogen stream with vigorous stirring; the mixture was kept under vacuum (400 mbar) and vigorous stirring at 60°C for 2 h. The films of this material were then obtained by casting the mixture on a glass plate and evaporating the solvent under vacuum (400 mbar) at 70°C. The films were extracted in Soxhlet with a CH_3OH/H_2O (6/1; v/v) solution and then vacuum dried at 70°C for 1 day. They were characterized by *FT*i.r.–attenuated total reflectance (a.t.r.) spectroscopy (i.r.: 1615 cm^{-1} (ureic C=O amide I), 1585 cm^{-1} (ureic C=O amide II)).

Films of N_2LL/PU blend. Films of N_2LL/PU blend were obtained by mixing 10 g of a 10% solution of PU in DMF with a methylene chloride solution containing 0.4 g of N_2LL polymer under nitrogen stream and vigorous stirring, following the chemical routes used to prepare films of crosslinked PU; then the material was washed in CH_2Cl_2. The film obtained was characterized by *FT*i.r.–a.t.r. spectroscopy (i.r.: 1634 cm^{-1} (amidic C=O amide I)).

MEASUREMENTS

FT*i.r. spectroscopy*

The *FT*i.r. spectra were obtained using a Perkin–Elmer M 1800 spectrophotometer connected to a Data Station 7500 professional computer. The a.t.r./*FT*i.r. spectra were recorded using a KRS5 crystal with an incident angle of 45°. Mercury cadmium telluride (MCT) and deuterated triglycine sulphate (DTGS) detectors were used and the apparatus was purged with nitrogen. The frequency scale was internally calibrated with a reference helium– neon laser to an accuracy of 0.01 cm^{-1}. Typically, 300 scans at a resolution of 2 cm^{-1} were averaged and the spectra were stored on floppy disk.

A Barnes microcircle cell for liquids equipped with germanium crystal was used to record the spectra in aqueous solution. The spectra of N_2LL in water solution at pH 12 and pH 3 were recorded between 3000 and 900 cm^{-1}. These pH values were chosen on the basis of the basicity constants[2] to record the spectra of the N_2LL polymer in the neutral and fully protonated forms.

Water uptake and permeability

Water uptake studies were carried out by dipping films of the different materials into 0.1 M NaCl solution or 1 M HCl solution. They were periodically removed, wiped with absorbent paper to eliminate surface liquid and weighed on a Mettler AC 100 digital balance. After several days the specimens approached a limiting weight which, within the precision of the balance, did not change significantly over a further period of 1 day. The percentage water uptake (*WU*) was calculated by comparing dry and wet sample weights:

$$WU(\%) = \frac{M - m}{m} \times 100$$

where M = wet sample weight and m = dry sample weight.

Permeability studies were carried out at room temperature in pure water; sheets of the tested materials swollen in water were fixed vertically at the centre of a 1 cm diameter diaphragm cell. Both sides of the cell were slowly stirred. For the permeation experiment one side of the cell was filled with pure water and the other with 0.4 M HCl aqueous solution. Permeation was followed by pH measurements.

The permeation of OH^- ions through sheets of protonated PUPA was studied by using a 0.5 M NaOH solution instead of 0.4 M HCl.

Estimation of basic nitrogen in the different samples of N_2LL. Samples of different materials previously dipped in hydrochloric acid solution and treated with 0.1 M NaOH were titrated with mercury nitrate solution according to the method previously described[4]. This method only permits an evaluation of the more superficial basic nitrogens.

Potentiometric measurements

Potentiometric titrations were carried out in a thermostated glass cell at 25°C, at a constant ionic strength of 0.1 M NaCl. A digital Radiometer PHM-84 potentiometer equipped with a Ross glass electrode (Orion, mod 81-01) and a Ross reference electrode (Orion, mod 80-05) were used together with a Metrohm Multidosimat piston burette connected to an Olivetti M20 computer. All the titrations were carried out using a cell filled with ≈100 ml of 0.1 M NaCl solution.

Before titrating PUPA samples and N_2LL surface grafted PU, a blank experiment was carried out; a 0.1 M NaCl solution containing a fine dispersion of native PU and a known amount of 0.1 M HCl solution was titrated with 0.1 M NaOH standard solution. PU fine dispersion did not change the titration curve. In fact, a typical strong acid–strong base curve was obtained.

N_2LL surface grafted PU. N_2LL surface grafted PU films were cut in such a way as to obtain a fine dispersion of the material in a 0.1 M NaCl aqueous medium. A known amount of standard HCl solution was then added to the above NaCl solution containing the sample, with magnetic stirring under a nitrogen stream, and was left until a steady state was reached (2 h). The titration was carried out with standard NaOH solution; after each addition (0.1 ml) the voltage of the solution was measured and recorded once a steady value was reached (generally 20 s). A curve with two inflexion points was obtained; the first point was relative to the titration of excess HCl and the second to the quantity of nitrogen atoms protonated. Back titration of the alkaline dispersion medium with HCl solution again gave a two inflexion point curve.

A direct titration of the sample in 0.1 M NaCl solution with HCl solution was also carried out. After each addition (0.1 ml) the voltage of the solution was measured and recorded once a steady value was reached (generally 20 s). A curve with only one inflexion point was obtained.

PUPA samples. The titrations of PUPA samples were carried out by the above procedure. The 0.1 M NaCl solution containing the sample in fine dispersion and a known amount of standard HCl solution was left under magnetic stirring and nitrogen stream until a constant e.m.f. was reached (1 day). During the titration with 0.1 M NaOH solution, the voltage reached a constant steady value in 15 min after each addition (0. 1ml). When the reading was taken after 20 s only the protons in excess were titrated and a typical strong acid–strong base curve was obtained.

The sample was then back titrated using a 0.1 M HCl solution and the time necessary to reach the steady voltage was still 15 min. Both the titration curves (*Figure 1*) showed two inflexion points, as in the case of N_2LL surface grafted PU discussed above.

Method of calculation. The basicity constants of N_2LL in the different bulks and in the free form were deduced from the titration curves (*Figure 2*) by a procedure similar to that already used for resins[3] and computed by the APPARK program on an Olivetti M20 computer. The amount of N_2LL (mmol) in the different materials, i.e. N_2LL surface grafted PU and PUPA, was obtained as the difference between the initial number of HCl mmoles and the mmoles of excess HCl calculated at the first equivalent point in the titration with NaOH. This amount corresponds to the difference calculated between the two equivalent points in the same curve. It is also equal to the difference between the two equivalent points in the HCl back titration curve.

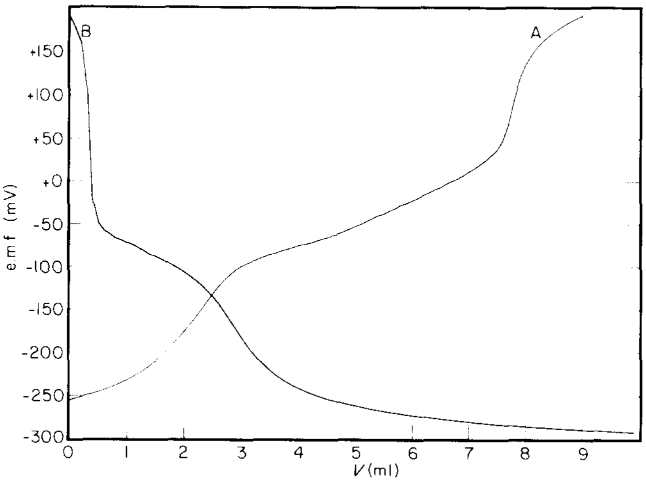

Figure 1 Potentiometric titration curves of a PUPA I sample with: (A) 0.1 M HCl solution; (B) 0.2 M NaOH solution (stabilization time 15 min)

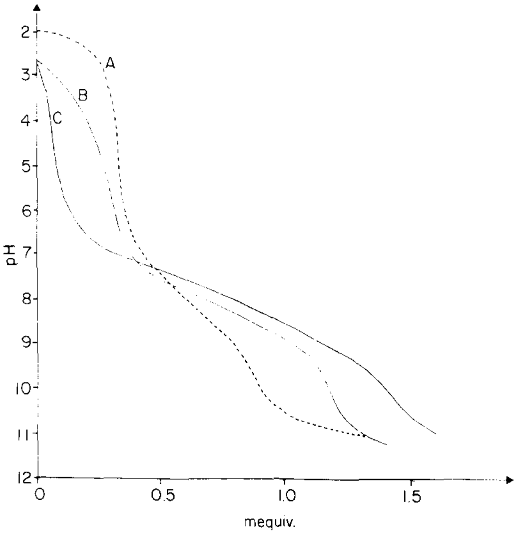

Figure 2 Potentiometric titration curves of: N_2LL polymer; (B) N_2LL surface grafted PU; (C) PUPA samples

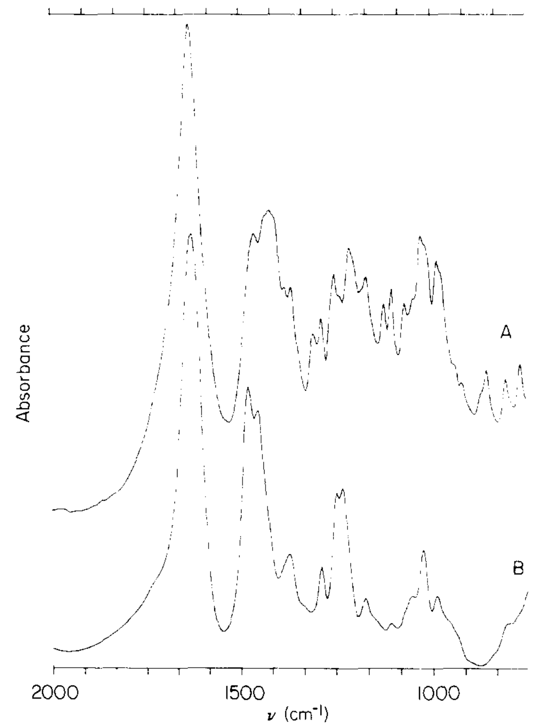

Figure 3 *FT*i.r. spectra in KBr of: (A) N_2LL polymer; (B) protonated N_2LL polymer

RESULTS AND DISCUSSION

FT*i.r. spectra*

Solid N_2LL. Spectra of solid N_2LL and N_2LL hydrochloride ($N_2LL^{H^+}$) in KBr pellets are shown in the 2000–750 cm^{-1} range in *Figure 3*. The assignments of the most important bands are reported in *Tables 1* and *2*.

The two spectra are similar, the main difference being the different intensities of some bands. However, the frequency shifts provoked by the presence of the positively charged groups in protonated N_2LL are small. For example, the C=O stretching shifts from 1632 to 1626 cm^{-1} due to the formation of stronger hydrogen bonds between the C=O groups and the protonated aminic nitrogens of N_2LL hydrochloride as previously observed[7]. The bands due to CH_2 and CH_3 bending occur in the 1480–1400 cm^{-1} range. The relative intensity and frequencies of these bands in the spectrum of $N_2LL^{H^+}$ (*Figure 3* and *Table 2*) are different from those of N_2LL (*Table 1*), due to the effect of the NH^+ group on the nearest CH_3 and CH_2. The positions of CH_3 and CH_2 symmetrical deformation frequencies are in fact sensitive to the electronegativity of the element to which they are attached[9]. The bands in the range 1290–1200 cm^{-1}, attributed to the CH_2 of the $-(CH_2)_4-$ chain wagging vibrations, are also affected by the protonation: they are

Table 1 *FT*i.r. frequencies (cm^{-1}) observed for unprotonated N_2LL in different bulks and their assignments

	N_2LL^a	N_2LLw^b	N_2LLg^c	N_2LL^c	N_2LLp^c
Urethane amide I					1725
Amide I	1632	1595	1638	1631	1623
$\left.\begin{matrix}CH_2\\CH_3\end{matrix}\right\}$bending	1461–1419	1478–1448	1459–1433	1459–1433	1465–1438
CH_2 wagging	1252–1226	1245–1230	1221	1225	1208
C–O–C stretching			1107	1108	

[a] KBr pellet
[b] At pH = 12
[c] Obtained from the difference spectrum

Table 2 *FT*i.r. frequencies (cm^{-1}) observed for protonated N_2LL in different bulks and their assignments

	$N_2LL^{H^+\,a}$	$N_2LLw^{H^+\,b}$	$N_2LL_g^{H^+\,c}$	$N_2LL_b^{H^+\,c}$	$N_2LL_p^{H^+\,c}$
Urethane amide I					1726
Amide I	1626	1612	1629	1629	1626
$\left.\begin{matrix}CH_2\\CH_3\end{matrix}\right\}$bending	1477–1450	1479–1450	1460–1435	1460–1447	1469–1444
CH_2 wagging	1245–1228	1245–1230	1222	1228	1200
C–O–C stretching			1107	1116	

[a] KBr pellet
[b] At pH = 3
[c] Obtained from the difference spectrum

weaker in the N_2LL spectrum than in that of $N_2LL^{H^+}$. These absorptions are weak in normal hydrocarbons, but become appreciably intense in compounds with polar end groups[10].

In aqueous solution (N_2LL_w). The spectra of N_2LL in solution at two different pHs (12.0 and 3.0) are shown in *Figure 4*. The assignments of the most important bands are summarized in *Tables 1* and *2*. The band relative to C═O stretching in the spectrum at pH 12.0 (N_2LL_w) is at 1595 cm^{-1}. The drop to a lower frequency with respect to the C═O frequency observed in the solid N_2LL spectrum ($\Delta\nu = 37$) is due to the strong interaction of the N–C═O group with water molecules[11]. This shift is less remarkable when compared with $N_2LL_w^{H^+}$ ($\Delta\nu = 14$) because the $NH^+\cdots O{=}C$ intrapolymer hydrogen bond present in the latter[7] reduces the possibility of interaction of the protonated form of the polymer with water molecules.

The bands in the 1480–1400 cm^{-1} range due to CH_2 and CH_3 bending occur at the same frequencies in both N_2LL_w and $N_2LL_w^{H^+}$, but they are more intense in the latter. They are shifted to higher frequencies with respect to those observed in the spectra of N_2LL and are very close to those of $N_2LL^{H^+}$.

The same behaviour is observed for the CH_2 wagging mode: the bands fall at about the same frequencies in $N_2LL_w^{H^+}$, N_2LL_w and $N_2LL^{H^+}$, but at lower frequencies than in N_2LL.

The absorption frequencies of the CH_2 and CH_3 bending modes are very sensitive to changes in the local conformation of these groups, whereas the absorption frequencies of the CH_2 wagging mode depend on both the length and the conformation of the chain since vibrations that involve the entire chain are delocalized[11]. The close similarity of the CH_2 and CH_3 bending and CH_2 wagging mode frequencies in the $N_2LL^{H^+}$, N_2LL_w and $N_2LL_w^{H^+}$ spectra means that the polymer assumes the same conformation in these three different states. Quantum chemical computations stress the reduction of

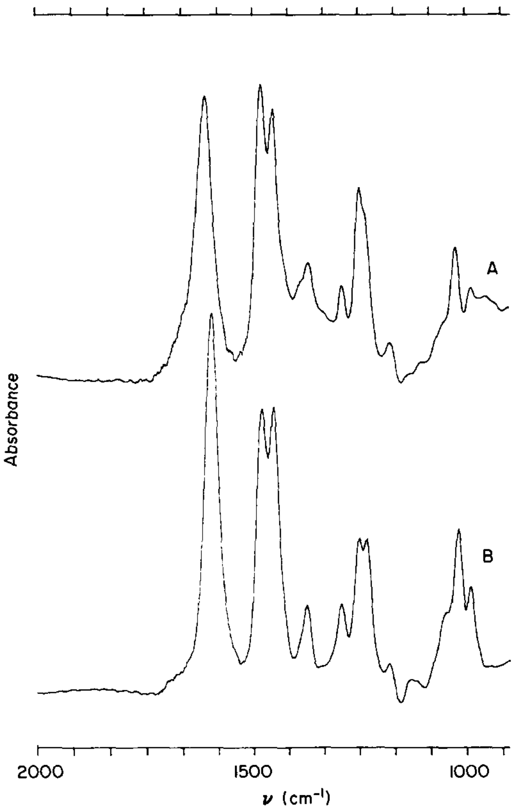

Figure 4 Difference spectra of N_2LL at: (A) pH 3.0; (B) pH 12.0

conformational freedom of the protonated N_2LL due to the formation of strong hydrogen bonds between onium ions and carbonyl groups belonging to the same monomeric unit. Furthermore, water molecules can form hydrogen bridges with the amidic and tertiary nitrogens group, imposing an ordering effect[7].

In different bulks. First we look at the neutral form. The spectra of N_2LL surface grafted polyurethane, N_2LL blended with polyurethane and PUPA are reported in *Figure 5*. The spectrum of N_2LL can be obtained as the difference spectrum by using the null criterion and minimizing the pure PU band at $1526\ cm^{-1}$ (amide II). Hence we obtain N_2LL_g, spectrum of N_2LL grafted PU minus the spectrum of HMDI grafted PU (*Figure 6A*); N_2LL_b, the spectrum of N_2LL blended with PU minus the spectrum of PU (*Figure 6B*); and N_2LL_p, the spectrum of PUPA minus the spectrum of PU chains crosslinked with HMDI (*Figure 6C*). Because of the subtraction method used only the most intense bands were taken into account and are reported in *Tables 1* and *2*.

A band at $1725\ cm^{-1}$ appears in the difference spectrum of N_2LL_p. This is absent in the other difference spectra, N_2LL_g and N_2LL_b. The presence of this band, attributed to the free C=O stretching of the urethane group[4], underlines the fact that the chains of polyurethane in PUPA are less involved in hydrogen bonds than in polyurethane alone or in PU crosslinked with HMDI. In fact the hydrogen bonded C=O stretching appears simultaneously as a negative band at $1700\ cm^{-1}$.

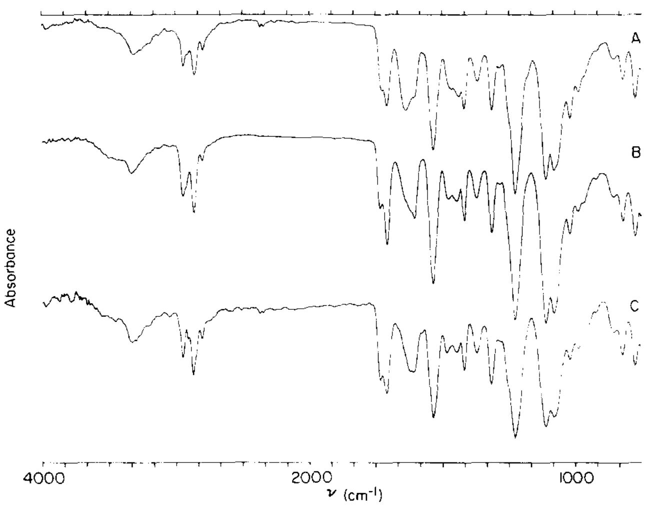

Figure 5 *FT*i.r.–a.t.r. spectra of: (A) N_2LL surface grafted PU; (B) N_2LL/PU blend; (C) PUPA I

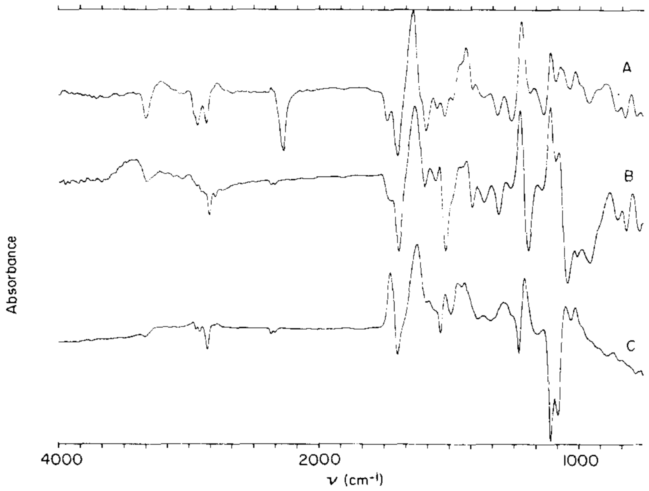

Figure 6 Difference spectra of N_2LL in: (A) N_2LL surface grafted PU (N_2LL_g); (B) N_2LL/PU blend (N_2LL_b); (C) PUPA I (N_2LL_p)

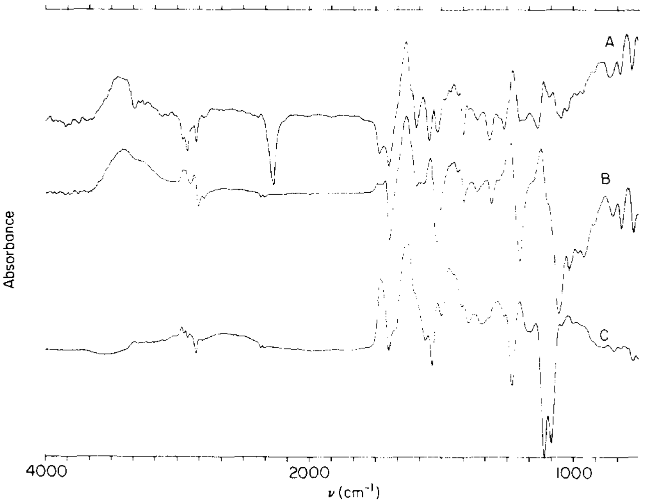

Figure 7 Difference spectra of protonated N_2LL in: (A) N_2LL surface grafted PU ($N_2LL_g^{H^+}$); (B) N_2LL/PU blend ($N_2LL_b^{H^+}$); (C) PUPA I ($N_2LL_p^{H^+}$)

The band of the free C–O–C group is present in both the N_2LL_g and N_2LL_b spectra but absent in the N_2LL_p spectrum. The band does not appear in the N_2LL_p spectrum because it was obtained by subtracting the spectrum of PU crosslinked with hexamethylenediisocyanate, in which the band is present, from the spectrum of PUPA, containing the free C–O–C band. This means that there is less possibility of the polyurethane chains in the three different bulks forming hydrogen bonds, i.e. the interaction of the polyurethane chains is reduced upon adding N_2LL to the polyurethane matrix, whether by merely mixing the two polymers in a blend (N_2LL_b) or by linking the N_2LL chains to the polyurethane chains via the hexamethylenediisocyanate bridge (N_2LL_p and N_2LL_g).

The band relative to the amide C=O stretching of N_2LL shifts to a lower frequency in the spectrum of N_2LL_g ($1638\ cm^{-1}$), N_2LL_b ($1631\ cm^{-1}$) and N_2LL_p ($1623\ cm^{-1}$). This means that the strength of the interaction of the N_2LL chains with the surroundings varies with the particular bulk and follows the trend $N_2LL_p > N_2LL_b > N_2LL_g$.

Now we consider the protonated form. A subtraction similar to that described above was adopted to obtain the spectrum of protonated N_2LL in the different bulks (*Figure 7*), from the corresponding protonated samples (*Figure 8* and *Table 2*). The amide I frequency decreases from N_2LL_g to $N_2LL_g^{H^+}$ and remains substantially the same in $N_2LL_{b,p}^{H^+}$ and $N_2LL_{b,p}$. The amide C=O groups of N_2LL_g are free enough to interact with the other polymeric chains or the rest of the macromolecule. Thus, in the protonated sample, they can interact with the positive charges of the protonated tertiary amino groups of the same monomeric unit, as occurs in protonated N_2LL in solution[7].

The other bands present in the spectra of protonated N_2LL in all the different bulks remains at almost the

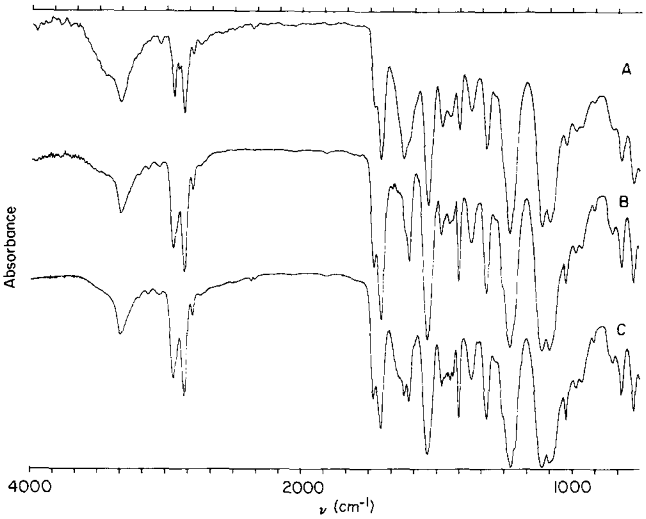

Figure 8 *FT*i.r.-a.t.r. spectra of protonated samples of: (A) N_2LL surface grafted PU; (B) N_2LL/PU blend; (C) PUPA I

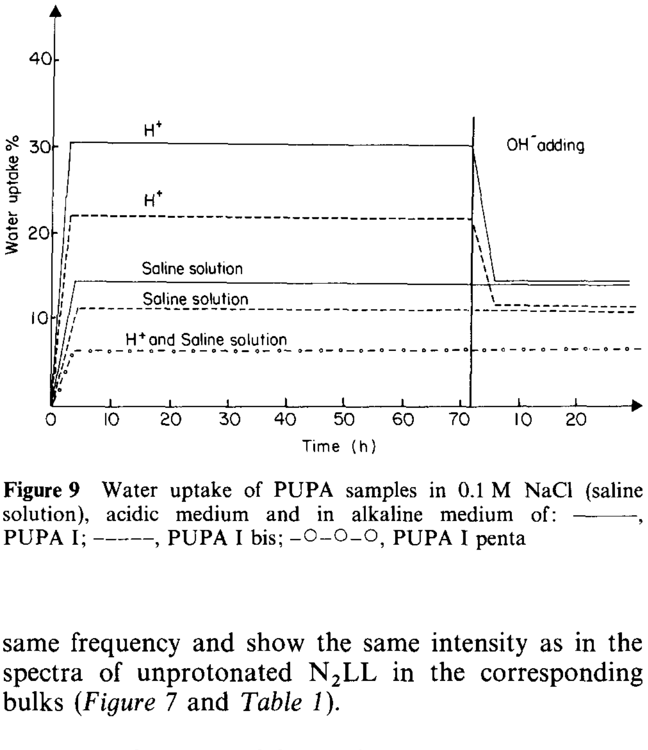

Figure 9 Water uptake of PUPA samples in 0.1 M NaCl (saline solution), acidic medium and in alkaline medium of: ———, PUPA I; – – – –, PUPA I bis; -o-o-o, PUPA I penta

same frequency and show the same intensity as in the spectra of unprotonated N_2LL in the corresponding bulks (*Figure* 7 and *Table 1*).

Water uptake, permeability and protonation constants

Figure 9 gives the water uptake of different PUPA materials, PUPA I, PUPA I bis and PUPA I penta, containing different percentages of N_2LL, in 0.1 M NaCl solution or an acidic medium. From *Figure 9* it is evident that the percentage water uptake depends on the composition of both solutions and PUPA materials. The water uptake of the PUPA samples is greater in an acidic medium than in 0.1 M NaCl, in the order PUPA I > PUPA I bis > PUPA I penta, in both media. PUPA penta, which contains the least N_2LL, gives the same percentage water uptake in 0.1 M NaCl and acidic solution. The water uptake of polyurethane is zero. If each PUPA sample, previously immersed in acidic medium, is soaked in alkaline solution the water uptake decreases and returns to the value obtained in 0.1 M NaCl.

This means that only the hydrophilic N_2LL polymer is responsible for water uptake both in NaCl and acidic solution. In the latter case the acidic medium provokes the protonation of the N_2LL chains, causing further adsorption of water.

Similar behaviour has been reported for resin with N_2LL[12]; the swelling of the resin was calculated in 0.1 M NaCl and 1.53 M sulphuric acid and was found to be greater in the latter.

The permeability of such materials to H^+ ions is reported in *Figure 10* and confirms the water uptake data. In this case the PUPA sample containing the largest proportion of N_2LL reaches the plateau in the shortest time, this time increasing with decreasing quantity of N_2LL (PUPA bis and PUPA penta). Protons do not penetrate samples of native PU. The protonation of the tertiary aminic nitrogens of N_2LL occurs progressively in HCl solution because the meshes enlarge, allowing further protonation. However, OH^- ions do not penetrate even if PUPA samples are protonated.

Samples of PUPA and N_2LL grafted polyurethane were titrated with HCl or back titrated with NaOH solution. The titration curves are shown in *Figure 2*. The protonation constants obtained for the N_2LL polymer free, in the resin, grafted on polyurethane and in PUPA are summarized in *Table 3* together with the *n* values of the Henderson–Hasselbalch equation.

Only two protonation constants were necessary to simulate the titration curves of N_2LL_g, N_2LL_p and N_2LL in resin form. The protonation constants of N_2LL surface grafted polyurethane and PUPA agree well with those previously found for N_2LL in the free form and in resin, except for the *n* values, but the greatest similarity was between N_2LL and N_2LL_g, and N_2LL in resin and N_2LL_p. This reflects the different environment of the N_2LL chains of the two classes of materials; the polymer shows the same mobility and assumes similar conformation when it is in the linear form (free N_2LL) or when it is anchored by one end to the surface of the polyurethane support (N_2LL_g). It behaves differently when both ends of the N_2LL chains are fastened (N_2LL in PUPA and in resin).

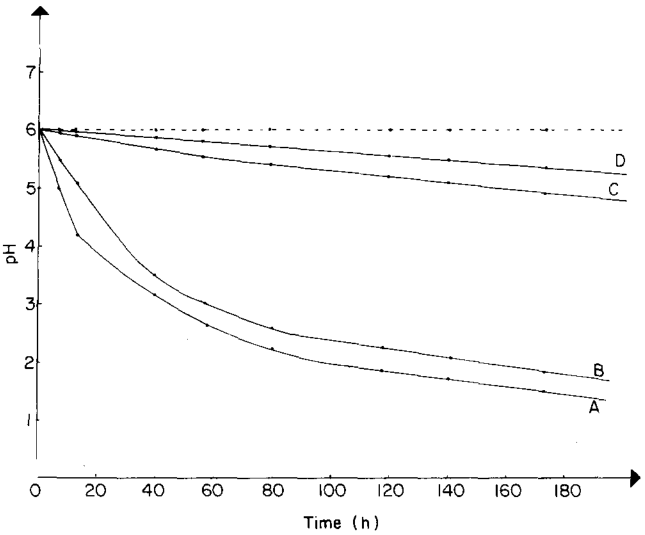

Figure 10 Proton permeability of: (A) PUPA I (7 μmol basic nitrogen cm^{-2}); (B) PUPA I (4 μmol basic nitrogen cm^{-2}); (C) PUPA I bis (1.6 μmol basic nitrogen cm^{-2}); (D) PUPA I penta (0.24 μmol basic nitrogen cm^{-2}); – – – –, PU

Table 3 Thermodynamic values for the protonation of N_2LL at 25°C in 0.1 M NaCl

Compound	Ionic strength (mol/dm^3) NaCl	Reaction	log $K^{\circ a}$	n^a	Reference
Free N_2LL	0.1	$L + H^+ \rightleftharpoons LH^+$	8.715	1	
		$LH^+ + H^+ \rightleftharpoons LH_2^+$	7.689	1	2
N_2LL in resin	0.1	$L + H^+ \rightleftharpoons LH^+$	8.58	1	
		$LH^+ + H^+ \rightleftharpoons LH_2^+$	7.44	1	3
N_2LL grafted PU, N_2LL_g	0.1	$L + H^+ \rightleftharpoons LH^+$	8.88 (21)	0.82 (22)	
		$LH^+ + H^+ \rightleftharpoons LH_2^+$	7.57 (20)	0.71 (18)	This paper
N_2LL in PUPA, N_2LL_p	0.1	$L + H^+ \rightleftharpoons LH^+$	8.55 (35)	0.93 (12)	
		$LH^+ + H^+ \rightleftharpoons LH_2^+$	7.38 (12)	0.71 (01)	This paper

$^a\log K = \log K^\circ + (n-1)\log(1-\alpha)/\alpha$

CONCLUSIONS

The interactions between N_2LL polymer and polyurethane chains are weak due to the different nature of the two polymers: polyurethane is hydrophobic, whereas N_2LL is a hydrophilic polymer. N_2LL_p interacts more strongly with polyurethane via hydrogen bonds than N_2LL_b or N_2LL_g. The closer interpenetration of the two polymers increases both the strength and the possibility of interaction. When in contact with water, the hydrophilic N_2LL chains prefer to interact with water than with PU. In fact, the N_2LL/PU blend separates in this solvent and the N_2LL polymer goes into solution.

In PUPA samples the N_2LL chains clearly remain anchored to the PU but their mobility is restored when they are surrounded by water molecules; they assume a behaviour similar to that of N_2LL free in solution, as confirmed by the protonation constant values. This explains why the polymer also complexes heparin in the network with PU.

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