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Thermodynamic and Spectroscopic Studies on the Protonation of an Optically Active Polyampholyte

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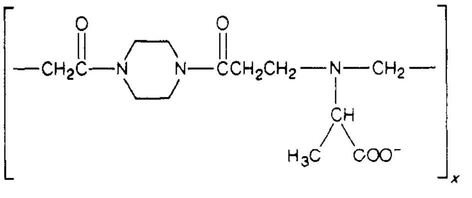
ABSTRACT: The protonation of an optically active polymer containing an α-alanine residue was studied in aqueous solution by spectroscopic (FT-IR, circular dichroism) and thermodynamic (potentiometric, calorimetric, viscometric) techniques. For the polyampholyte, which undergoes a conformational transition in the alkaline region, both basicity constants follow the modified Henderson-Hasselbalch equation. log K_1 relative to the protonation of the tertiary nitrogen atom decreases with α (the degree of protonation of the whole macromolecule) while the uptake of the proton from the carboxylate group is greatly facilitated as the number of negative charges on the macromolecule decreases. Similar behavior was also observed in polyampholytes of comparable structure. Circular dichroism and FT-IR spectral examination strongly supports an interaction between the protonated nitrogen and the carbonyl groups which gives rise to a locally ordered structure involving the optically active center in the dissymmetrical perturbation.

Introduction

Up to now extensive studies on poly(amido amine)s have been carried out in aqueous solution.[1] The repeating units of the polymers, containing basic nitrogens shielded by diacryloylpiperazine groups, show basicity constants independent of each other. All the thermodynamic functions (ΔG°, ΔH°, and ΔS°) are thus "real".[2]

Recently it was seen that the presence of carboxylate groups, as a pendant to the main chain, leads to loss of independence of the monomeric units.[3] The charged COO^- groups evidently affect the electrostatic field force created on the chain. A similar effect was not observed in poly(amido amine)s carrying uncharged amino or hydroxyl groups as side substituents.[4]

Thermodynamic studies on polyamido polymers containing ω-amino acid residues revealed a polyelectrolyte effect; the basicity constants vary with the degree of protonation α (ref 3) in a manner dependent on the length of the aliphatic chain between the amino nitrogen and the carboxylate group,[5] but the enthalpy changes of both basic groups are independent of the degree of protonation. The polyelectrolyte behavior is thus due only to entropy effects. The approach of the incoming protons to the basic center with the formation in one case of the zwitterionic form $L-H^+$ (L^- being the monomeric unit of the macromolecule) in the first step, with a consequent decrease in size of the macromolecular coil, and the role of the hydrophobic chain have not been fully investigated. In order to understand the mechanism of protonation of these polymers, we synthetized a new polyampholyte containing an optically active amino acid (L-alanine) in the backbone of the macromolecule. The particular structure of L-PAAA$_1$ allows us to study the influence of the hydrophobic group on the protonation and to carry out conformational studies in aqueous solution with spectroscopic (CD, FT-IR) and the classical potentiometric and calorimetric techniques.



L-PAAA$_1$

Results and Discussion

Basicity Constants. Both the basicity constants, log K°_i (i = 1, 2), relative to the protonation of the tertiary aminic nitrogen and carboxylate group, respectively, of L-PAAA$_1$ are reported in Table I together with the corresponding n_i values. The latter figures take into account the polyelectrolyte effect and can be regarded as an index of accessibility of the proton to the basic group as the protonation reaction proceeds.

Both the basicity constants follow the modified Henderson-Hasselbalch equation[6]

$$\log K_i = \log K^\circ_i + (n - 1) \log [(1 - \alpha)/\alpha]$$

The log K°_1 values of L-PAAA$_1$ is higher than that of the polyamido polymer containing glycine residue (PAAA$_1$) in the macromolecule but closely resembles the value of the polymer carrying a β-alanine residue (PAAA$_2$, Table I). The presence of a methyl group in α-position increases the basicity of the glycine residue as occurs in simple α-amino acids,[7] due to the electron-donating properties. Moreover, the presence of the methyl group seems to affect the polyelectrolyte properties in the same way as in the homologous PAAA$_2$ compound. Not only are the log K°_1's equal, but the corresponding n_1 values (>1) are very close, reflecting a similar difficulty in protonation of the tertiary basic nitrogen as protonation proceeds. The protonation of a whole negatively charged macromolecule leads to a neutralization of charge and then to a decrease in the electrostatic field force. Zwitterionic species are thus formed as in simple α-amino acids and the previously considered polyampholytes, resulting in a more compact structure.[3] This is more evident in a salt-free water solution in which the electrostatic field increases, determining higher log K°_1 and n_1 values (Table I).

The protonation of the carboxylate groups has quite a different behavior. log K°_2 is higher for PAAA$_1$ than for PAAA$_2$.[3] The corresponding n_2 value is <1 as occurs for PAAA$_1$ but lower in magnitude. It means that the approach of the incoming protons to the COO^- groups in the zwitterionic form ($^+HN\ COO^-$) becomes easier and easier as the degree of protonation of the whole macromolecule increases, i.e., as the number of zwitterionic groups in the macromolecule decreases. Of all the PAAA$_n$ series[3] containing ω-amino acid residues, compact conformation of the zwitterionic form was only attributed to PAAA$_1$.[3] This behavior seems to be generalized because it is found in all cases in which the basic COO^- group being protonated is in the α-position with respect to other basic groups.[3,8] The n value less than 1 can be considered diagnostic of a tightly compact conformation which uncoils during protonation.

The basicity of the COO^- group increases in salt-free water solution, as occurs for small molecular weight car-

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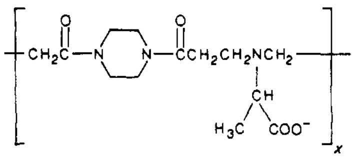
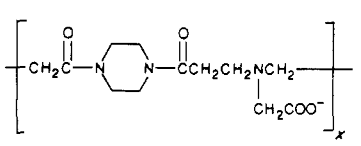
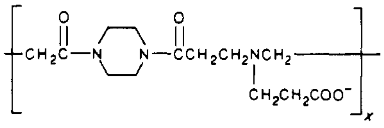
Table I
Thermodynamic Values for the Protonation of Polyamido Polymer Containing Amino Acid Residues at 25 °C in 0.1 M NaCl and in Salt-Free Water

compd	ionic strength, mol/dm^3	reactn	α-range	log $K°_i$[a]	n_i[a]	$-\Delta G°_i$,[b] kcal/mol	$-\Delta H°_i$, kcal/mol	$\Delta S°_i$,[b] cal/mol·K
 L-PAAA$_1$	0.1	$L^- + H^+ \rightleftharpoons LH^\pm$	0.1–0.8	8.52 (4)	1.12 (3)	11.62 (5)	7.5 (1)	13.8 (5)
		$LH^\pm + H^+ \rightleftharpoons LH_2^+$	0.1–0.7	2.34 (12)	0.57 (8)	3.2 (2)	0.6 (2)	9 (1)
	0.0	$L^- + H^+ \rightleftharpoons LH^\pm$	0.1–0.8	9.00	1.35			
		$LH^\pm + H^+ \rightleftharpoons LH_2^+$	0.1–0.8	3.02	0.52			
 PAAA$_1$	0.1	$L^- + H^+ \rightleftharpoons LH^\pm$	0.2–0.8	8.30	1.07	11.32	7.62	12.4
		$LH^\pm + H^+ \rightleftharpoons LH_2^+$	0.1–0.4	2.01	0.80	2.74	0.60	7.2
 PAAA$_2$	0.1	$L^- + H^+ \rightleftharpoons LH^\pm$	0.2–0.7	8.52	1.14	11.62	8.64	10.0
		$LH^\pm + H^+ \rightleftharpoons LH_2^+$	0.2–0.7	3.57	1.23	4.87	2.57	7.7

[a] log K_i = log $K°_i$ + $(n - 1)$ log $(1 - \alpha)/\alpha$. [b] Values calculated at $\alpha = 0.5$. See ref 3 and 18 for PAAA$_1$ and PAAA$_2$.

boxylic acids,[9] but the n value remains almost unchanged. The n_2 value can be considered to be related to the tendency of protons to neutralize a negative COO$^-$ charge in an atmosphere of the polyampholyte chain. Hence the compact configuration assumed by the L-PAAA$_1$ in the zwitterionic form, with partial charge neutralization, reduces the electrostatic contribution to protonation and renders the n_2 parameter similar to that obtained in 0.1 M NaCl.

Viscosity. A viscometric titration of L-PAAA$_1$ in 0.1 M NaCl solution at 25 °C is reported in Figure 1 along with the distribution curves of the different ionized species. The titration was performed by adding sodium hydroxide solution stepwise to a fully protonated polymer solution. At low pH values a net positive charge is present on the macromolecule in the LH$_2$$^+$ form and this determines electrostatic repulsion between the monomeric units which stiffens the macromolecule. On addition of OH$^-$, the reduced viscosity decreases until a critical minimum value is reached. This value corresponds to the maximum amount of the zwitterionic species in which the polymer is present as a compact coil due to the internal neutralization of charges. As OH$^-$ uptake proceeds, the zwitterionic state vanishes and a steep increase in η_{sp}/C is observed during the liberation of the protonated nitrogen, which provokes a continuous extension of the macroion because of the presence of charged COO$^-$ groups.

The minimum at the isoelectric point in other examples of poly(amido amino acid)s is not as marked as in L-PAAA$_1$.[3] The L-PAAA$_1$ polymer with the α-alanine residue seems to behave in a slightly different way because of the methyl group, which renders the macromolecule more hydrophobic and apt to assume a more compact coil conformation.[10]

Circular Dichroism (CD). CD measurements of L-PAAA$_1$ were performed in both 0.1 M NaCl and salt-free water solutions. Figure 2 shows an example of the CD spectra of L-PAAA$_1$ in aqueous solution at 25 °C and at two different pHs over a wavelength range of 200–300 nm. The CD pattern is typical of polypeptides having a random coil conformation[11] so the positive peak found at 215 nm was assigned to the n–π^* amide transition.[12] At low pH values the spectra are very similar to those of poly(glutamic acid) and poly(L-lysine) in their charged state.[13,14]

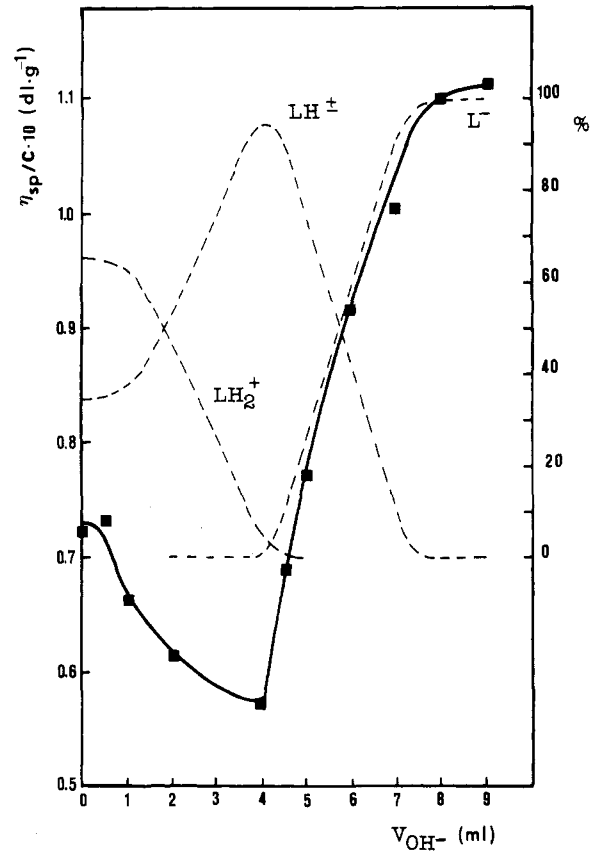


Figure 1. Reduced viscosity (η_{sp}/C) of polymer L-PAAA$_1$ in 0.1 M NaCl solution (■) versus volume of added OH$^-$. Distribution curves (dashed lines) of the various ionized species calculated from the basicity constants in 0.1 M NaCl.

In Figure 3 the molar ellipticity $[\theta]$ at 215 nm is plotted against pH for 0.1 M NaCl and salt-free water solutions. The carbonyl group lies near the piperazine ring and though the optically active center positioned in the L-alanine residue is a little far, it is reasonable to believe that

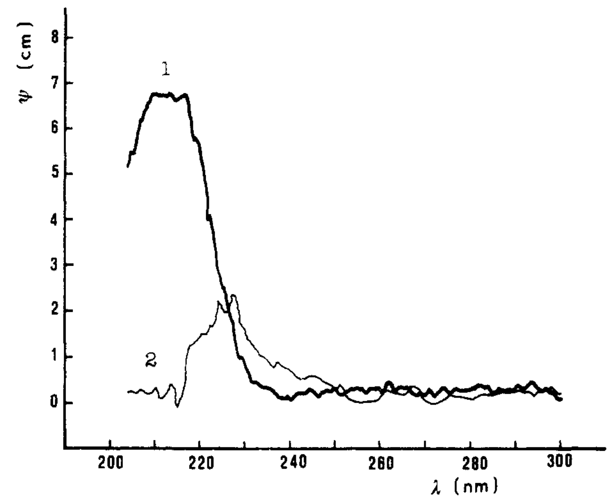


Figure 2. Circular dichroism spectra of polymer L-PAAA$_1$ in 0.1 M NaCl solution at pH 2 (curve 1) and pH 11 (curve 2). (Sensitivity S = 0.5 mdeg/cm.)

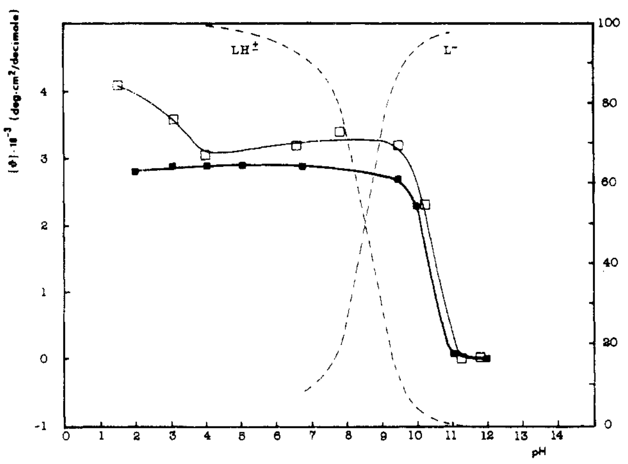


Figure 3. pH-induced conformational transition of polymer L-PAAA$_1$ in 0.1 M NaCl (■) and in salt-free water (□) solutions. Molar ellipticity [ϑ], at 215 nm, is plotted versus pH (full lines). Distribution curves of L$^-$ and LH$^{\mp}$ species calculated from the basicity constants in 0.1 M NaCl (dashed lines).

in the LH_2^+ form the protonated nitrogen also interacts with the C═O groups of the backbone until the zwitterionic form is retained. This hypothesis is in agreement with previous results obtained by theoretical calculation.[2] The interaction creates a locally ordered structure, even if the whole macromolecule lies in the coil form. This structure is destroyed by deprotonation of the NH$^+$ group at increasing pH. The polymer passes to free forms with a sharp conformational change in a narrow pH range as a result of the change in net charge. Superimposed distribution curves show the effects of the charge state in this transition (Figure 3).

A similar pattern was also observed in poly(N^ϵ,N^ϵ-dicarboxymethyl-L-Lysine), an ampholytic homopolypeptide, which presents a coil with locally extended structure at neutral pH, vanishing to other random coils in the alkaline or acidic regions.[15,16] Ionic strength had negligible effects on the CD spectra of our system. Simple NaCl salt slightly lowers the intensity of the CD spectrum without altering the wavelength of the transition.[17] Also in a methanol/water mixture, only a slight increase in molar ellipticity is observed, confirming that this solvent stabilizes the locally ordered coil conformation.[15]

FT-IR Spectra. The spectra of L-PAAA$_1$ were recorded at three different pHs (2, 6, and 11.5). The main frequencies observed are reported in Table II with their assignments. These pHs were chosen on the basis of the log K values as determined above and correspond to predominantly LH_2^+ diprotonated, LH$^{\mp}$ monoprotonated (zwitterionic), and L$^-$ unprotonated forms, respectively.

Table II
Frequencies (cm^{-1}) Observed for the L-PAAA$_1$ Polymer in Aqueous Solution at Different pHs and Their Assignments

pH 2	pH 6	pH 11.5	assignments
1715			C═O stretch of COOH group
		1675	amide I
1610	1610		amide I and antisym COO$^-$ stretch of dipolar ion
		1590	antisym COO$^-$ stretch
1565	1565	1565	amide II
1475	1475	1475	CH$_2$ bend
1450	1450	1450	CH$_3$ antisym def
	1405	1405	sym COO$^-$ stretch
1370	1370	1370	CH$_3$ sym def
1285	1285	1285	amide III
1245	1245	1245	C–O stretch + O–H bend
1020	1020	1020	piperazinic ring

Table III
Stretching Frequencies (cm^{-1}) of the COOH, $^+$HN COO$^-$, COO$^-$, and NC═O Groups as a Function of pH

	stretching frequencies[a]			
pH	COOH	NC═O	COO$^{-\,b}$	COO$^{-\,c}$
2	$1715_{m,br}$	1610_{vs}		
6		1610_{vs}	1610_{vs}[d]	1405_{w}
11.5		1675_{m}	1590_{vs}[e]	1405_{m}

[a] vs = very strong; m = medium; w = weak; br = broad. [b] Antisymmetric stretching of COO$^-$. [c] Symmetric stretching of COO$^-$. [d] Antisymmetric stretching of COO$^-$ in the dipolar form. [e] Antisymmetric stretching of COO$^-$ in the anionic form.

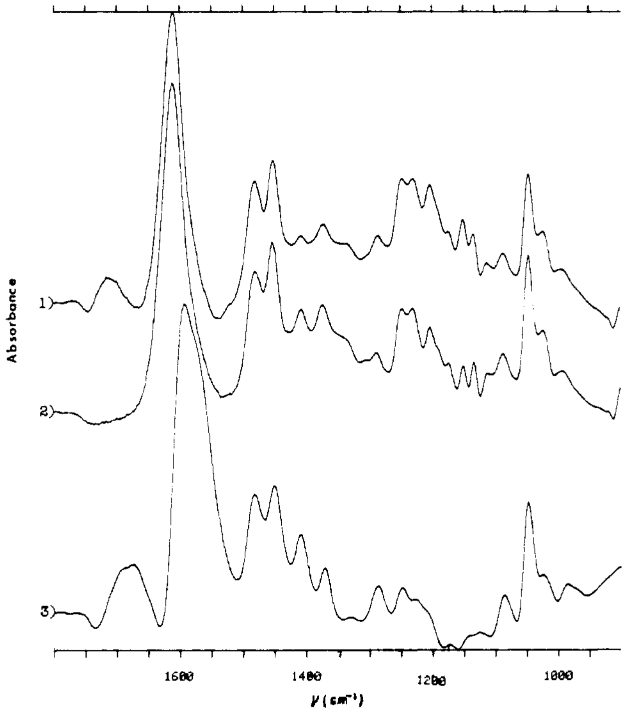


Figure 4. FT-IR difference spectra of polymer L-PAAA$_1$ at different pH values: pH 2 (curve 1), pH 6 (curve 2), and pH 11.5 (curve 3).

The largest variations in the spectra of the polymer are observed in the region between 1800 and 1500 cm^{-1} (Figure 4), where the changes in carboxyl group (COOH), symmetric and antisymmetric stretching of the carboxylate ion (COO$^-$), and the stretching of the amidic group (NC═O) are particularly significant. The assignments of the frequencies relative to these groups are summarized in Table III. The band at 1715 cm^{-1}, corresponding to the stretching of the COOH carboxyl group,[18] is present only at the lowest pH. At this pH there is also a strong band at 1610 cm^{-1} due to the stretching of the amidic group (NC=O). This band occurs in L-PAAA$_1$ at 1675 cm^{-1} at pH 11.5 (see below). Therefore the shift to lower frequencies of the amide I band is explained by the interaction between the C=O of the amidic group and the protonated aminic group in the main chain (as shown also by CD measurements). As a matter of fact, polymers in a random coil conformation without interaction between the several repeating units show an amide I band in the range 1670–1680 cm^{-1}.[19,20]

At pH 6 a strong band may be observed again at 1610 cm^{-1}. It can be attributed to both the amide I and the antisymmetric stretching of the COO$^-$ in the dipolar ($^+$HN COO$^-$) form,[21] because the zwitterionic form is the predominant species in solution at this pH. At this pH the symmetric stretching of the carboxylate ion is also evident (the weak band at 1405 cm^{-1}). At the highest pH the predominant species is L-PAAA$_1$ in the anionic form, and separation of amide I from the COO$^-$ antisymmetric stretching absorption frequency is observed. In fact at this pH the NC=O group does not interact with other charged groups, shifting the amide I band to a higher frequency, corresponding to the characteristic absorption frequency of the polymer in aqueous solution.[19,20] The band arising from the antisymmetric stretching of the carboxylate ion (COO$^-$) shifts from 1610 to 1590 cm^{-1}, i.e., to a lower frequency, as is also observed in the simple amino acids.[21]

Enthalpy and Entropy Changes. The protonation of both basic groups (N and COO$^-$) in the monomeric unit of the L-PAAA$_1$ polymer is an exothermic effect and both $-\Delta H^\circ_i$ values are independent of the degree of protonation. Thus the variation in $-\Delta G^\circ_i$ values is due only to entropy contributions. Table I summarizes the thermodynamic functions obtained at 25 °C in 0.1 M NaCl.

The $-\Delta H^\circ_1$ value of L-PAAA$_1$ refers to the protonation of the basic tertiary nitrogen in the alanine residue and agrees with that of PAAA$_1$.[18] The first protonation step leads the macromolecule to a compact structure due to the interaction of the COO$^-$ group and the two C=O amidic groups with the protonated nitrogen, as revealed by the CD and FT-IR measurements. The interaction of the two distant amidic groups with the central protonated nitrogen determines a contraction in the coil of the polymer, which explains the steep decrease in the reduced viscosity upon passing from the L$^-$ to the LH$^{\mp}$ form. Similar behavior was observed in the other poly(amido amino acid)s.[3] The further protonation of LH$^{\mp}$ to LH$_2$$^+$, in which the interaction of the NH$^+$ group with the two C=O groups remains, provokes only a moderate increase in viscosity, not apparent in the PAAA$_n$ series.

If we consider the structure of L-PAAA$_1$ with a methyl group out of the pendant chain and compare it to PAAA$_1$, we can attribute the behavior of L-PAAA$_1$ to a larger contraction of the polymer in the zwitterionic form for a larger hydrophobic contribution. This also explains the larger entropy contribution than for PAAA$_1$. The more compact conformation of the polymer provokes a greater liberation of water molecules reflected in the larger ΔS° value.

The protonation of the carboxylate ion of L-PAAA$_1$ also occurs with an enthalpy effect equal to that of the protonation of the carboxylate in PAAA$_1$ but with a larger entropy effect. This means that the higher basicity constant of L-PAAA$_1$ is due only to entropy effects. These are also responsible for the anomalous behavior of these polymers, namely, increased basicity with increasing protonation of the macromolecule. The $\Delta S_2/\alpha$ slope of L-PAAA$_1$ is also steeper than that of PAAA$_1$, indicating that the liberation of water molecules during the overall protonation process is enhanced.

Experimental Section

Synthesis. The L-PAAA$_1$ polymer was prepared as previously reported for homologous polyampholytes[3] starting from 1,4-diacryloylpiperazine (2.50 g, 0.0129 mol) and an equimolecular amount of simple amino acid (1.16 g, 0.0130 mol of L-alanine, from Merck) dissolved in water (5 mL) containing triethylamine (2.20 mL, 0.0157 mol).

The mixture was allowed to react under an inert atmosphere for 3 weeks at room temperature with occasional stirring. Then the mixture was stirred for 2 h on Amberlite IRC-50 (15 g, from Sigma) to eliminate (C$_2$H$_5$)$_3$NH$^+$. The centrifuged solution was dried in vacuo. The viscous product was dissolved in methanol and precipitated in an excess of diethyl ether. The white solid was washed three times with fresh ether and dried in vacuo: yield, 2.00 g; intrinsic viscosity at 30 °C, $[\eta]$ = 0.13 dL/g in CH$_3$OH/H$_2$O (90/10 v/v %) mixture.

^{1}H NMR was found consistent with the proposed structure, and elemental analysis and potentiometric purity (86%) were consistent with a structure comprising two water molecules for each monomeric unit (C$_{13}$H$_{21}$N$_3$O$_4$·2H$_2$O): Anal. Calcd C, 48.9; H, 7.9; N, 13.1. Found C, 49.2; H, 8.1; N, 12.6.

Potentiometric Measurements. Potentiometric titrations were performed by using a Ross reference electrode (Model 80-05) and a Ross glass electrode (Model 81-01) connected to a digital PHM-84 radiometer potentiometer. All titrations were carried out in a constant-temperature cell at 25 °C. Presaturated nitrogen was kept over the surface of the polymer solution to prevent carbon dioxide adsorption. The basicity constants in 0.1 M NaCl were determined by the addition of 0.1 mol dm^{-3} NaOH to an aqueous polymer solution containing a large excess of hydrochloric acid. In salt-free water the polymer solution was first titrated with 0.1 M HCl and then back-titrated with 0.1 M NaOH solution. All polymer solutions were prepared immediately before use.

The data obtained were printed and stored on the floppy disk of an M20 Olivetti computer programmed to control the experiments.

The experimental details of the potentiometric titrations are summarized in Table IV. The APPARK program, which was used to calculate the protonation constants, has been described elsewhere.[6]

Viscometric Measurements. The viscometric titrations were performed by adding step by step small amounts of 0.1 M NaOH to a polymer solution contained in a Cannon Ubbelohde 50 E 998 viscometer having a flow time of 210 s for aqueous 0.1 M NaCl at 25 °C. Corrections for kinetics energy and rate of shear were found to be negligible.

A weighed amount of polymer (ca. 110 mg) was dissolved in 0.1 M NaCl, and a known amount of 0.1 M HCl was added to give an acidic polymer solution (25 mL total volume).

Pure CO$_2$-free water was used throughout, and the solutions were used immediately after preparation. The percentages of the different ionic species in solution were computed by means of the FITH program as described elsewhere.[6] The intrinsic viscosity was determined at 30 °C by stepwise dilution of the polymer solution with the solvent (methanol/water mixture) and extrapolating the η_{sp}/C values at zero concentration by means of the least-squares method.

CD Measurements. Circular dichroism measurements were carried out on a Jasco J500 A spectropolarimeter which directly records the dichroic optical density ψ (the difference in absorbance between left- and right-handed circularly polarized radiation). The molar ellipticity $[\theta]$ is given by the relation

$$[\theta] = \frac{10^{-3}\psi SM}{dC} \qquad (\text{deg·cm}^2/\text{dmol})$$

where ψ (mdeg) is peak height in cm, S (mdeg/cm) is the sen-

Table IV
Experimental Details of the Potentiometric Measurements for L-PAAA$_1$ Polymer

reactn	10^3T_L,[a] mol	$10^3T_{H^+}$,[b] mol	C_T,[d] mol/dm^3	pH range	α range	correl coeff	log $K°_i$	n_i
			In 0.1 M NaCl at 25 °C[c]					
$L^- + H^+ \rightleftharpoons LH^\pm$	0.2431	1.2951	0.1737	7.89–9.06	0.22–0.78	0.9998	8.479 (2)	1.097 (5)
$LH^\pm + H^+ \rightleftharpoons LH_2^+$				2.30–2.86	0.20–0.71	0.9437	2.431 (7)	0.49 (2)
$L^- + H^+ \rightleftharpoons LH^\pm$	0.1674	0.8112	0.0761	8.19–9.54	0.11–0.68	0.9994	8.569 (3)	1.108 (7)
$LH^\pm + H^+ \rightleftharpoons LH_2^+$				2.40–2.75	0.20–0.49	0.9970	2.387 (2)	0.583 (5)
$L^- + H^+ \rightleftharpoons LH^\pm$	0.2859	0.8322	0.1265	7.82–8.88	0.32–0.80	0.9998	8.508 (1)	1.166 (3)
$LH^\pm + H^+ \rightleftharpoons LH_2^+$				2.39–2.80	0.12–0.34	0.9970	2.212 (3)	0.651 (5)
			In Salt-Free Water at 25 °C[e]					
$L^- + H^+ \rightleftharpoons LH^\pm$	0.2043	0.2043	0.1084[f]	—	—	—	—	—
$LH^\pm + H^+ \rightleftharpoons LH_2^+$				2.82–3.60	0.11–0.79	0.9750	3.011 (6)	0.51 (1)
$L^- + H^+ \rightleftharpoons LH^\pm$	0.2043	0.7463	0.1265	8.24–10.22	0.10–0.78	0.9996	8.999 (3)	1.35 (1)
$LH^\pm + H^+ \rightleftharpoons LH_2^+$				2.82–3.66	0.11–0.79	0.9710	3.019 (8)	0.53 (2)

[a] Initial amount of ligand. [b] Initial amount of hydrogen ions. [c] Average $\log K_1 = 8.52 + 0.12 \log (1 - \alpha)/\alpha$, $\log K_2 = 2.34 - 0.43 \log (1 - \alpha)/\alpha$. [d] NaOH titrant concentration. [e] Average $\log K_1 = 9.00 + 0.35 \log (1 - \alpha)/\alpha$, $\log K_2 = 3.02 - 0.48 \log (1 - \alpha)/\alpha$. [f] Hydrochloric acid titrant concentration.

Table V
Experimental Details of the Calorimetric Measurements for the L-PAAA$_1$ Polymer in 0.1 M NaCl at 25 °C

reactn	10^3T_L, mol	$10^3T_{H^+}$, mol	C_T,[d] mol/dm^3	pH range	α range	$-\Delta H°$, kcal/mol	points[a]
$L^- + H^+ \rightleftharpoons LH^\pm$	0.1238	0.2886	0.1265	8.25–9.37	0.63–0.14	7.46 (8)	8
	0.2239	0.2239	0.1265	7.76–9.64	0.82–0.09	7.48 (17)	19
	0.1702	0.1702	0.0766	7.84–9.63	0.80–0.09	7.46 13)	23
						av 7.47 (13)[b]	
$LH^\pm + H^+ \rightleftharpoons LH_2^+$	0.2236	0.0000	0.1084[e]	2.94–2.39	0.09–0.44	0.54 (23)	20
	0.1238	0.2886	0.1265	2.27–2.40	0.57–0.45	0.57 (20)	10
						av 0.56 (22)[c]	

[a] Number of points from titration curve. [b] $\Delta H°_1$. [c] $\Delta H°_2$. [d] NaOH titrant concentration. [e] HCl titrant concentration.

sitivity of the instrument, d (dm) is the optical path length, C (g/100 mL) is the polymer concentration, and M is the molecular weight of the monomeric unit. In our experimental conditions (S = 0.5 mdeg/cm, d = 1 mm), C/M refers to the molar concentration of the residue amide groups (two for each monomeric unit). CD measurements on polymer solutions at various pH values were carried out, preparing each solution by mixing aliquots of the mother solution with the appropriate solvent (0.1 M NaCl or salt-free water of known pH value). The pH of the polymer solutions was measured with a combined glass microelectrode (mod 81-03 Orion). A CD fused-quartz optical cell was used throughout. CD measurements at different ionic strengths and methanol/water mixtures were performed as above.

FT-IR Measurements. FT-IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer M1800 between 3000 and 900 cm^{-1}. A MCT detector was used and the apparatus was purged with nitrogen. Typically 300 scans at a resolution of 2.0 cm^{-1} were averaged and the spectra stored on magnetic disk. The frequency scale was internally calibrated with a reference helium–neon laser to an accuracy of 0.01 cm^{-1}. A Barnes microcircle cell for liquid with a germanium crystal was used to record the spectra in an aqueous solution. The concentration of the polymer solution used was about 4×10^{-2} M. The pH values of the solution were adjusted by adding a small amount of aqueous HCl or aqueous NaOH solution.

Spectral Digital Processing. A Perkin-Elmer 7500 data station was used to obtain difference spectra of the polymer–water system. The water subtraction from the polymer solution was made with the null criterion, trying to minimize the water band.

Calorimetric Measurements. Continuous calorimetric titrations were carried out in the isothermal mode with a Tronac calorimeter, Model 1250. The procedure and the calorimetric apparatus have previously been described.[6] Polymer solutions in 0.1 M NaCl were titrated at 25 °C in a 25-mL stainless steel reaction vessel with hydrochloric acid or sodium hydroxide solutions by using a Gilmont buret at a 0.0833 mL·min^{-1} delivery rate.

The measurements were controlled by a North Star CCP 930 computer running the THERMAL program and the $-\Delta H°$ values were evaluated with the FITH program[6] on the M24 Olivetti computer connected to the North Star for the "data files" transfer.

Table V summarizes the experimental details for the protonation enthalpies of the polymer.

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Registry No. ((L)-Alanine)(1,4-diacryloylpiperazine) (copolymer), 119771-14-1; ((L)-alanine)(1,4-diacryloylpiperazine) (SRU), 119771-15-2.

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Interfacial Structure and Dynamics of Macromolecular Liquids: A Monte Carlo Simulation Approach

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ABSTRACT: Dynamic Monte Carlo simulations are performed on a dense liquid consisting of freely jointed, 20-bead long chain molecules in a cubic lattice in the vicinity of solid walls. The objective is to elucidate the equilibrium structure and dynamic behavior of polymer melts at interfaces. Elementary bead moves are chosen so as to mimic the process of conformational isomerization. Three different solid surfaces are studied: (I) a strongly attractive surface with high potential barriers between adsorption sites that inhibit the lateral motion of adsorbed beads; (II) an equally strongly attractive surface with no barriers; (III) a weakly attractive surface with low potential barriers between sites. The microscopic structure of the polymeric liquid is significantly affected by the presence of solid walls. Segment density is enhanced near the strongly attractive surfaces and depleted near the weakly attractive surfaces. The distribution of chain centers of mass is peaked at a distance slightly less than one radius of gyration from the solid. Chain shapes are pronouncedly flattened adjacent to a solid wall and gradually assume unperturbed bulk characteristics as one moves away from the wall. The self-diffusion coefficient of chains, evaluated by monitoring their mean-squared center of mass displacement as a function of simulation time, is dramatically reduced near strongly adsorbing walls; on the contrary, chain mobility is enhanced near weakly adsorbing walls. The spatial dependence of self-diffusivity is highly correlated with, but not exclusively governed by, the behavior of local segment density in the interfacial region. The diffusive motion of chains is inherently anisotropic near a surface. Potential barriers between strongly attractive surface sites have only a minor effect on the self-diffusivity. The longest relaxation time of chains is determined as a function of their center of mass position by analyzing the long-time behavior of the end-to-end distance vector autocorrelation function. Strong segment–wall attraction prolongs relaxation times in the surface region appreciably, in comparison to the bulk. Moreover, potential barriers to the lateral motion of adsorbed segments exert a profound influence on the rate of molecular relaxation. Adding such barriers to a strongly attractive surface can cause the relaxation time of chains located near the surface to rise by as much as 80%.

1. Introduction

Interfaces between macromolecular liquids and solids play a key role in many technical applications. Gaining insight into the interfacial structure and dynamics of chain molecules in the solventless, condensed state will enhance our ability to design materials systems with controlled adhesion, wetting, and lubrication characteristics. Recent experimental evidence[1] indicates that substrate/polymer interactions can drastically influence the quality of products obtained by melt processing operations, such as extrusion and film blowing, through the phenomena of wall slip and melt fracture. On a more fundamental level, we wish to understand dynamic surface forces exhibited by neat, low molecular weight polymer liquids confined between closely spaced solid surfaces. Such forces have been measured recently by Horn and Israelachvili.[2]

The equilibrium and dynamic characteristics of a macromolecular liquid in the vicinity of a solid surface are expected to depart significantly from those of the unconstrained bulk. Adsorptive interactions between chain segments and sites on the surface and entropic constraints imposed on the propagation of chains at a phase boundary strongly influence local density, conformation, mobility, and relaxation. All these aspects vary with distance from the solid surface, on a length scale comparable to chain dimensions. The ensuing local property profiles govern the macroscopically manifested interfacial behavior of the polymer liquid.

Previous modeling work on bulk polymers at interfaces has focused on structural and thermodynamic properties. A lattice-based self-consistent mean field approach[3,4] has been useful in predicting bond orientation, chain shape, and density distribution, as well as surface and interfacial tension. A Monte Carlo simulation of the free surface of a polymer melt was recently presented by Madden,[5] who employs a highly efficient pseudokinetic algorithm to sample configuration space; it, too, invokes a lattice representation of the polymer. Lattices afford considerable simplification in dealing with the complicated configuration space of multichain systems, while at the same time they can preserve the basic physics of the problems at hand. More recently, a lattice Monte Carlo simulation has been performed by Ten Brinke et al.[6] on a polymer film confined between two nonadsorbing solid surfaces. Kumar et al.[7] report structural features obtained by Monte Carlo in a similar model system, using a continuum representation of the polymer.

Our interest here is in developing a simulation approach that can provide information not only on structural but also on *dynamic* characteristics of macromolecular liquids

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