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Spectroscopic and Calorimetric Studies on the Protonation of Polymeric Amino Acids

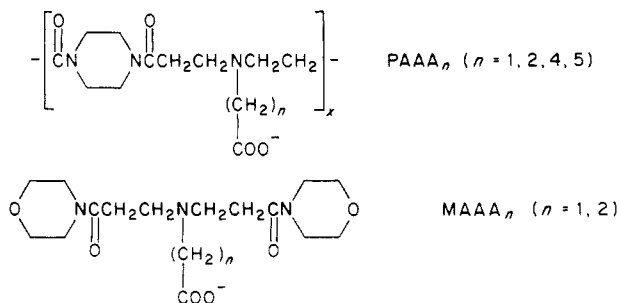
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ABSTRACT: The protonation of some poly(amido amines) has been studied in aqueous solution by FTIR spectrophotometry and by calorimetry. On the basis of the stretching bands of both the ionized and the un-ionized carboxyl groups, the structures of all four polymeric amino acids in their different protonation states are determined. Calorimetric studies show that the enthalpies of protonation do not change with pH and follow a trend similar to that observed in simple amino acids of comparable structure. An anomalously high value of $|\Delta H_2^\circ|$ observed for the polymer obtained by the polyaddition of β -alanine to diacryloylpiperazine has been found and attributed to the formation of a very highly symmetrical structure when the carboxyl groups are in the un-ionized form.

Introduction

In previous papers we have reported the synthesis, the protonation, and Cu^{2+} ion complexing behavior of a series of polymeric amino acids with a poly(amido amine) backbone and the corresponding nonmacromolecular models, having the following structure:



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These studies are performed by potentiometric, viscosimetric, and spectrophotometric techniques.¹ To better elucidate the mechanism of protonation of these polymers, we have now carried out spectroscopic and calorimetric studies. The spectroscopic studies have been performed by FTIR techniques in water.

Experimental Section

Materials. The syntheses of polymers PAAA₁, PAAA₂, PAAA₄, and PAAA₅ have been previously described.¹ The corresponding nonmacromolecular models MAAA₁ and MAAA₂ were synthesized in a similar way as previously reported.²

A CO₂-free NaOH solution was prepared, stored, and standardized as described elsewhere.³ Stock solutions of 0.1 M NaCl were prepared from sodium chloride (Suprapur Merck) and used without further purification as the ionic medium for calorimetric measurements.

FTIR Spectra. Transmission infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer M1500 with a nitrogen purge. Typically 250 scans at a resolution of 3.2 cm⁻¹ were averaged and the spectra were stored on a microfloppy disk. The frequency scale of the instrument was internally calibrated by

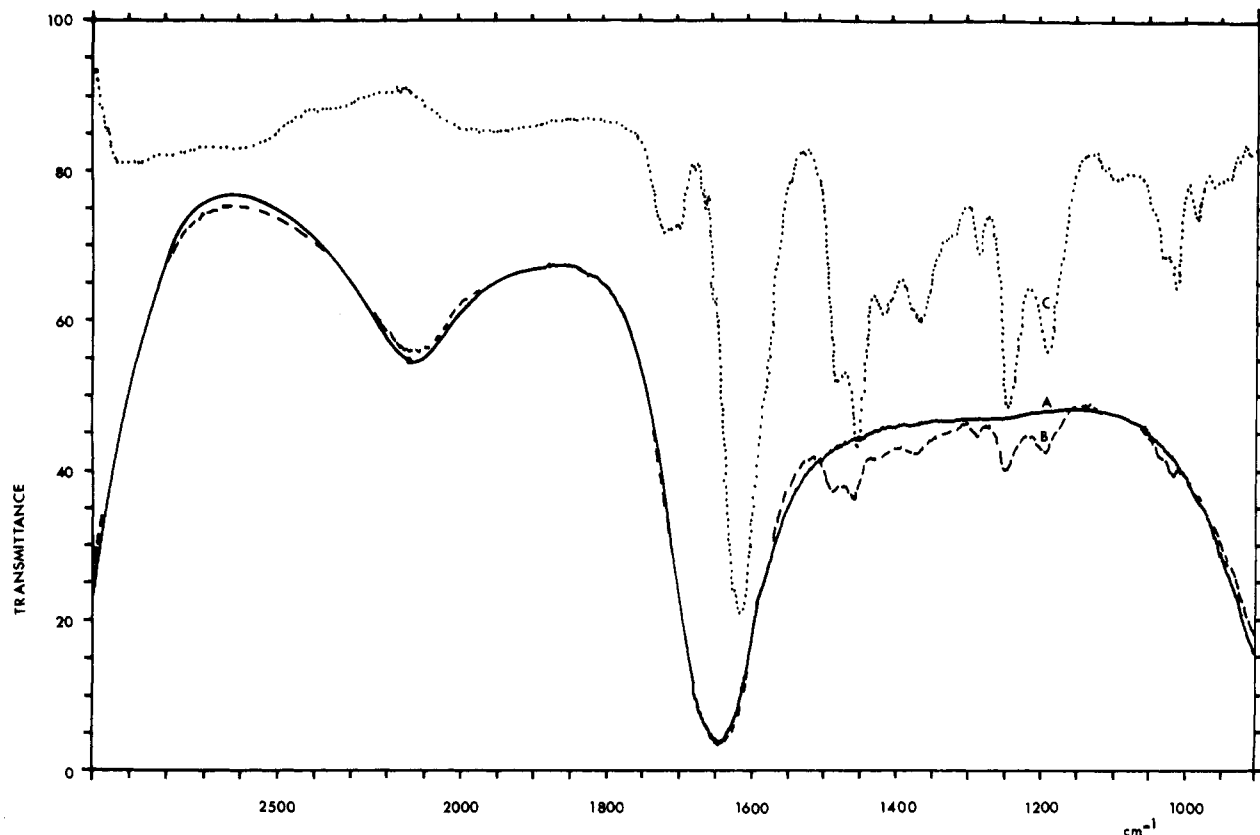


Figure 1. Water digital subtraction process for polymer PAAA₂ at pH 3: (A) — water spectrum; (B) --- spectrum of solution; (...) spectrum resulting from the subtraction (B-A) multiplied by a factor of 3.

a reference He-Ne laser to an accuracy of 0.01 cm⁻¹. We have used a cell for liquid with BaF₂ windows and path lengths of about 13 μm to record the spectra in aqueous solution.

The concentration of the polymer solution used was about 0.2 M.

The pH values of the solutions were adjusted by the addition of a small amount of aqueous HCl or aqueous NaOH solution.

Spectral Digital Processing. The Perkin-Elmer 3600 data station has been used to obtain difference spectra of polymer-water systems. Figure 1 illustrates the spectral subtraction procedure utilized in this work. The water absorption at the 1640-cm⁻¹ band overlaps some of the polymer bands. The water subtraction from the polymer solution was made with the null criterion trying to minimize the water band. We have obtained a high quality of subtraction spectra, and as a rule, no smoothing procedure was needed.

Calorimetric Measurements. The calorimetric titrations were carried out as previously described⁴ with a Tronac calorimeter operating in the isothermal mode. Solutions of all polymeric amino acids and the two nonmacromolecular models in the form of the sodium salts were titrated with HCl solution at 25 °C. Titrations were also performed by adding NaOH solution to a solution containing a weighed amount of polymeric amino acid dissolved in an acidified 0.1 M NaCl solution. Heats of dilution were determined by the addition of titrant to 0.1 M NaCl solution in the absence of polymer, while the heat of ionization of water at 25 °C in 0.1 M NaCl was taken from the literature.⁵

Experimental details for the protonation of the polymers and nonmacromolecular models are given in Table I. Only the calorimetric titration data in the region of constant temperature have been used for the computation of protonation enthalpies. The ΔH° values were computed with the FITH program described elsewhere.⁴

Results and Discussion

FTIR Spectroscopic Studies. The main frequencies observed for the polymers in aqueous solution at three different pH's are reported in Table II. These frequencies have been determined at pH 2, 5, and 9 for PAAA₁ and

Table I
Heats of Protonation: Experimental Details of
Calorimetric Measurements at 25 °C in 0.1 M NaCl

compd	pH range	C _T ^a mol dm ⁻³	T _L ^b mmol	T _H ^c mmol	no. points ^d
PAAA ₁	8.65-1.99	0.5150	0.6346	0	32
	7.46-9.23	-0.1259	0.1700	0.3311	10
	5.26-1.72	0.5150	0.9395	0.9395	29
PAAA ₂	3.29-9.77	-0.1259	0.1590	0.3201	32
	9.01-2.61	0.5150	0.6626	0.	32
					32
PAAA ₄	3.71-9.63	-0.1253	0.1602	0.3213	32
	8.96-2.97	0.5150	0.1655	-0.0009	32
PAAA ₅	3.72-9.51	-0.1253	0.1601	0.3212	32
	8.98-2.90	0.5150	0.6482	0	32
MAAA ₁	8.57-1.92	0.5150	0.6457	0	28
MAAA ₂	8.74-2.42	0.5150	0.6128	0.0031	27

^a Titrant concentration (negative values indicate titrations with NaOH). ^b Initial amount of ligand. ^c Initial amount of hydrogen ions. ^d Number of data points from titration curve.

pH 3, 6, and 9 in the other cases (Figure 2). These pH's have been chosen on the basis of the log *K* values previously determined for the same polymers¹ and correspond to prevalently diprotonated, monoprotated (zwitterionic), and unprotonated forms, respectively (Table III). The variation of the frequencies relative to the stretching of the carboxyl group (-COOH), symmetric and antisymmetric stretching of the carboxylate ion (-COO⁻), and stretching of the amidic (N-C=O) group is particularly significant. The assignments of the frequencies relative to these groups are reported in Table IV. They are quite similar to those previously observed in simple amino acids in aqueous solution.⁶ It may be observed that the band corresponding to the stretching of the carboxyl group is present only at the lowest pH. The relative frequency decreases from 1737 cm⁻¹ for PAAA₁ to 1710 cm⁻¹ for

Table II
Frequencies Observed for Polymer PAAA_n in Aqueous Solution at Different pH's^a

PAAA ₁			PAAA ₂			PAAA ₄			PAAA ₅		
pH 2	pH 5	pH 9	pH 3	pH 6	pH 9	pH 3	pH 6	pH 9	pH 3	pH 6	pH 9
1737 mbr			1710 mbr			1705 mbr			1703 m		
1616 vs	1617 vs	1604 vs	1617 vs	1612 vs	1603 vs	1614 vs	1613 vs	1601 vs	1614 vs	1614 vs	1601 vs
			1580 sh	1583 sh	1563 sh	1554 m	1554 vs	1552 vs	1550 m	1550 vs	1548 vs
1485 s	1482 s	1482 s	1481 s	1481 s	1481 s	1480 s	1478 s	1479 s	1480 s	1476 s	1476 s
1451 s	1451 s	1451 s	1454 s	1452 s	1450 s	1452 s	1452 s	1448 s	1454 s	1452 vs	1448 s
			1418 m	1420 sh		1418 m	1420 sh	1420 sh	1414 m	1418 sh	1420 sh
1398 sh	1398 m	1404 m		1405 m	1405 m		1408 s	1410 s		1408 s	1410 s
1370 m	1369 m	1371 m	1367 m	1378 br	1369 sh	1361 m	1365 mbr	1369 m	1365 m	1366 m	1369 m
1340 br	1347 br	1330 br	1330 br			1330 br	1330 br	1325 br	1335 br	1325 br	1320 br
1287 m	1287 m	1287 m	1290 m	1287 m	1287 m	1285 m	1287 m	1287 m	1287 m	1285 m	1288 m
1251 s	1249 m	1249 m	1250 s	1247 s	1247 m	1248 s	1250 s	1247 m	1250 a	1250 s	1248 m
1230 sh	1232 sh	1230 m		1229 m	1229 m	1232 sh	1232 sh	1227 m	1232 sh	1230 sh	1227 m
1198 m	1198 m	1198 sh	1196 s	1190 s	1194 sh	1194 m	1194 m		1194 m	1192 m	
1175 sh	1176 sh	1173 w	1175 sh	1174 sh	1174 sh	1174 m	1174 m	1174 sh	1171 m	1170 m	1172 m
1100 wbr	1100 wbr	1125 br	1100 wbr	1100 wbr	1128 br	1100 mbr	1102 m	1125 wbr	1102 wbr	1100 br	1125 br
1051 sh	1050 sh	1050 sh	1033 sh	1031 sh	1049 sh	1051 sh	1051 sh	1051 w	1050 sh	1050 sh	1050 sh
1025 m	1022 m	1017 m	1018 m	1018 m	1016 m	1022 m	1022 m	1014 m	1022 m	1022 m	1018 m
987 w		987 w	987 w	988 w	987 w	990 br	987 w	987 w	989 w	989 w	990 w

^a Abbreviations used in the Table for intensity; vs is very strong, s is strong, m is medium, w is weak, sh is shoulder, and br is broad.

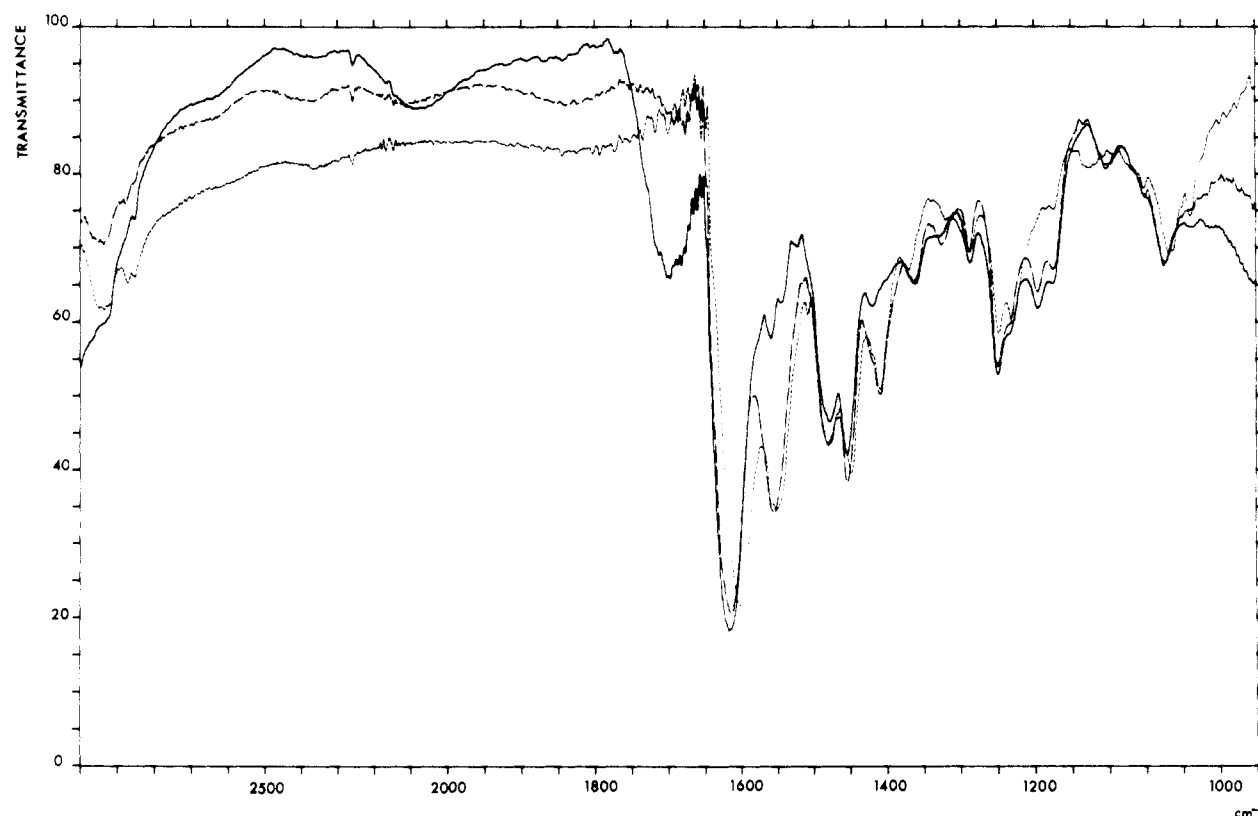
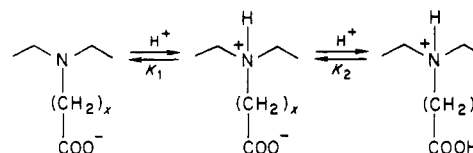


Figure 2. Spectra of polymer PAAA₄ at different pH's: (—) pH 3; (---) pH 6; (···) pH 9.

PAAA₂ to 1705 cm⁻¹ for PAAA₄ and then remains practically constant passing from PAAA₄ to PAAA₅. This is due to the inductive effect of the charged basic nitrogen in the chain, which obviously decreases by increasing the number of methylenic groups in the side chain.

The band corresponding to the antisymmetric stretching of the carboxylate ion is present also at the lowest pH, because of the presence, to a lesser extent, of the zwitterionic form. This is resolved in PAAA₂, PAAA₄, and PAAA₅ (Figure 3). The frequency of PAAA₂ remains practically constant passing from pH 3 to pH 6 and then decreases by 20 cm⁻¹ passing to pH 9. Also in this case this is probably due to the inductive effect of the protonated aminic group. At the highest pH this group is obviously unprotonated.

Table III
Basicity Constants of Polymeric Amino Acids at 25 °C in 0.1 M NaCl



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

compd	x	log K ₁ [°]	n ₁	log K ₂ [°]	n ₂
PAAA ₁	1	8.30	1.07	2.01	0.80
PAAA ₂	2	8.52	1.14	3.57	1.23
PAAA ₄	4	8.47	1.10	4.21	1.12
PAAA ₅	5	8.50	1.16	4.28	1.08

Table IV
Stretching Frequencies (cm^{-1}) of the Carboxyl Group ($-\text{COOH}$), the Carboxylate Ion ($-\text{COO}^-$) and the Amidic Group ($\text{N}=\text{C}=\text{O}$) of Polymeric Amino Acids as a Function of pH

polymer	pH	stretching frequencies ^a			
		$-\text{COOH}$	$\text{N}=\text{C}=\text{O}$	$-\text{COO}^-$ ^b	$-\text{COO}^-$ ^c
PAAA ₁	2	1737 m, br	1616 vs		1398 sh
	5		1617 vs		1398 m
	9		1604 vs		1403 m
PAAA ₂	3	1710 m, br	1617 vs	1580 sh	
	6		1612 vs	1583 sh	1405 m
	9		1603 vs	1563 sh	1405 m
PAAA ₄	3	1705 s	1614 vs	1554 m	
	6		1613 vs	1554 vs	1408 s
	9		1601 vs	1552 vs	1410 s
PAAA ₅	3	1703 s	1614 vs	1550 m	
	6		1614 vs	1550 vs	1408 s
	9		1601 vs	1548 vs	1410 s

^a vs is very strong, s is strong, m is medium, w is weak, sh is shoulder, and br is broad. ^b Antisymmetric stretching. ^c Symmetric stretching.

The frequencies of the same band for PAAA₄ and PAAA₅ are practically independent of pH, owing to the larger distance between basic nitrogen and carboxylate ions. It may be observed that this frequency (about 1550 cm^{-1}) is significantly lower than that of the corresponding band of PAAA₂ at higher pH. This trend in the frequencies of the bands relative to the stretching of carboxylate ions is similar to that observed in case of simple amino acids.⁷ The symmetric stretching of carboxylate ions lies at about 1400 cm^{-1} and is practically independent of pH, except for its absence at the lowest pH, where this species is present in a negligible amount. The frequency of the band relative to the stretching of the amidic $\text{N}=\text{C}=\text{O}$ group is practically the same for all the polymers considered, if compared at the same pH. In all cases it drops from about 1617 to 1602 cm^{-1} in passing from pH 6 to pH 9. This is again attributed to the inductive effect of the protonated aminic nitrogen, which is obviously the same in all cases. It may be observed that when both protonated and unprotonated nitrogens are present along the macromolecular chain, two bands relative to the stretching of the amidic $\text{N}=\text{C}=\text{O}$ should be observed.⁸ However, the distance (about 12 cm^{-1})⁸ is too small and the bands too broad to be resolved in aqueous solution. The frequencies of these polymers observed as a function of pH seem to demonstrate that no conformational transitions occur. It may be noted that Raman and IR spectra had been previously used to show conformational transition either in

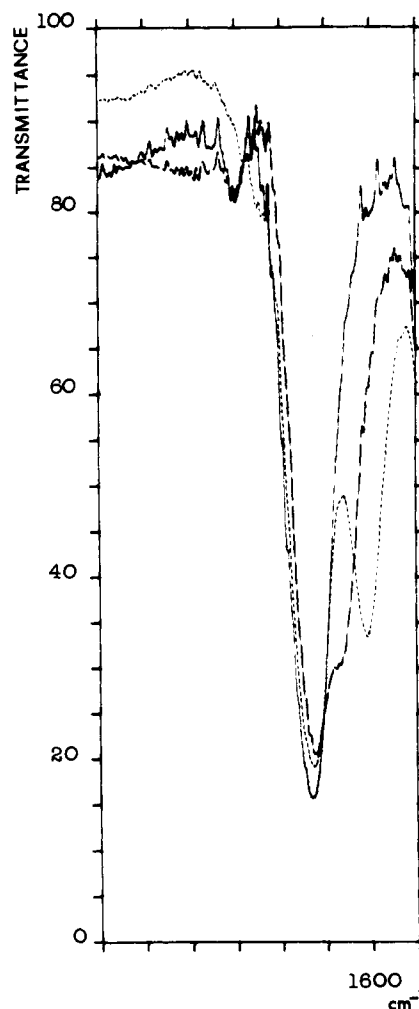


Figure 3. Spectra of PAAA₁ (—) at pH 5, of PAAA₂ (---) at pH 6, and of PAAA₄ (···) at pH 6 in the range $1850\text{--}1500\text{ cm}^{-1}$.

synthetic⁹ or natural polymers.^{10,11}

Calorimetric Studies. The thermodynamic functions of all polymeric amino acids with the two nonmacromolecular analogues are summarized in Table V. The enthalpy changes are "real" in all the series and do not follow the trend observed for the $\log K$'s. This means that the variation of the basicity constants with pH is entirely due to entropy effects, as observed in other previous cases.⁴ It means that the decrease in viscosity observed when the polymer passes from the L^- to L^-H^+ species¹ is connected with a change of the polymer chain from an expanded to a more compact random coil without altering the

Table V
Thermodynamic Values for the Protonation of Polymeric Amino Acids and Two Nonmacromolecular Models at 25°C in 0.1 M NaCl ^a

comps	$\text{CH}_3\text{---}(\text{CH}_2)_x\text{---}\text{N}^+\text{H}(\text{CH}_2)_x\text{---}\text{COO}^- \xrightleftharpoons{K_1} \text{CH}_3\text{---}(\text{CH}_2)_x\text{---}\text{N}^+\text{H}_2\text{---}\text{COO}^-$		$\Delta S_1^\circ, ^b \text{ cal mol}^{-1} \text{ K}^{-1}$	$\text{CH}_3\text{---}(\text{CH}_2)_x\text{---}\text{N}^+\text{H}(\text{CH}_2)_x\text{---}\text{COO}^- \xrightleftharpoons{K_2} \text{CH}_3\text{---}(\text{CH}_2)_x\text{---}\text{N}^+\text{H}(\text{CH}_2)_x\text{---}\text{COOH}$		$\Delta S_2^\circ, ^b \text{ cal mol}^{-1} \text{ K}^{-1}$
	$-\Delta G_1^\circ, ^b \text{ kcal mol}^{-1}$	$-\Delta H_1^\circ, \text{ kcal mol}^{-1}$		$-\Delta G_2^\circ, ^b \text{ kcal mol}^{-1}$	$-\Delta H_2^\circ, \text{ kcal mol}^{-1}$	
PAAA ₁	11.32(3)	7.62(5)	12.4(3)	2.74(1)	0.60(5)	7.2(2)
PAAA ₂	11.62(3)	8.64(4)	10.0(2)	4.87(5)	2.57(7)	7.7(4)
PAAA ₄	11.55(3)	8.83(6)	9.1(3)	5.74(1)	0.25(8)	18.4(3)
PAAA ₅	11.59(1)	9.17(5)	8.1(2)	5.84(1)	0.07(7)	19.4(3)
MAAA ₁	11.17(3)	7.53(2)	12.2(2)	2.59(7)	0.72(2)	6.3(3)
MAAA ₂	11.23(1)	8.68(2)	8.6(1)	4.88(1)	2.52(1)	7.9(1)

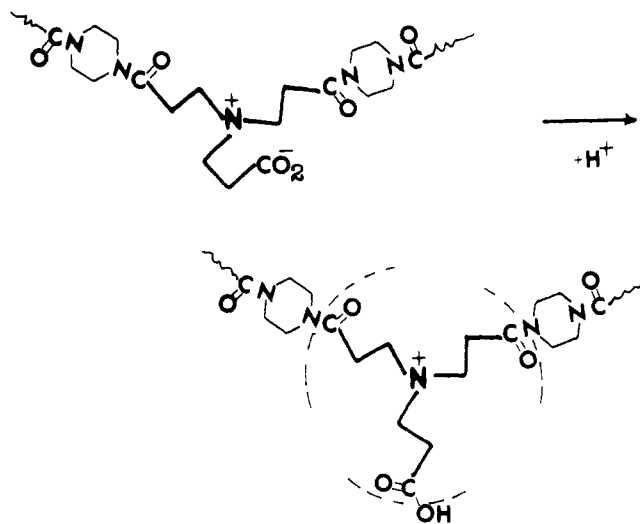
^a Values in parentheses are the standard deviations. ^b For the polymers these values were calculated at $\alpha = 0.5$.

"symmetry" of the monomeric unit, as suggested by the spectroscopic results (see above).

The ΔH_1° value, corresponding to the protonation of the tertiary nitrogen atom, is lower than that of the corresponding primary nitrogen of simple amino acids,¹²⁻¹⁴ but follows a similar trend with a regular increase of the enthalpy changes with the lengthening of the aliphatic chain. The ΔH_2° of protonation of the -COO^- group diminishes along the series by passing from PAAA₁ to PAAA₅, except for the PAAA₂ polymer, which shows a ΔH_2° larger than expected (Figure 4).

The same exothermic change is observed in the corresponding nonmacromolecular model MAAA₂ (see Table V), which does not appear in the case of the simple amino acid.¹¹⁻¹⁴ We think that this behavior is due to the highly symmetrical and energetically more favored structure reached by protonation of the -COO^- group in the PAAA₂ case.

The presence at the extremes of three identical C=O groups and a positive charge in the middle, after the proton is transferred from the solvated hydroxonium ion to the nitrogen, could give rise to a new and more stable orientation of water molecules around the symmetrical protonated species. The solvent molecules would be arranged rigidly on this particular structure by giving a further favorable energy term that only depends on the water-water electrostatic interaction. Indeed such a solvation order created by symmetrical structures was used to explain the enthalpy changes of other polyamines.¹⁵



The fact that ΔS° , instead of remaining constant, decreases by increasing the protonation degree of the whole macromolecule (Figure 4) is a strong indication that the liberation of water molecules on protonation not only involves the hydration shell of the unit that is being protonated but also, at least to some extent, involves the whole macromolecule.

The entropy change on protonation of the aminic groups slightly decreases with the length of the side chain (Table V).

On the contrary, the entropy change on protonation of the carboxylate groups strongly depends on the number of methylenes between the carboxyls and the aminic groups. Specifically the ΔS_2° is larger in the case of PAAA₄ and PAAA₅ compared to PAAA₁ and PAAA₂ and follows a "regular" trend, as in most polymeric acids,¹⁶ decreasing on increasing the degree of protonation.

The case of PAAA₁ is exceptional, since ΔS_2° increases with the degree of protonation. This means that the contribution of the whole macromolecule to the entropy

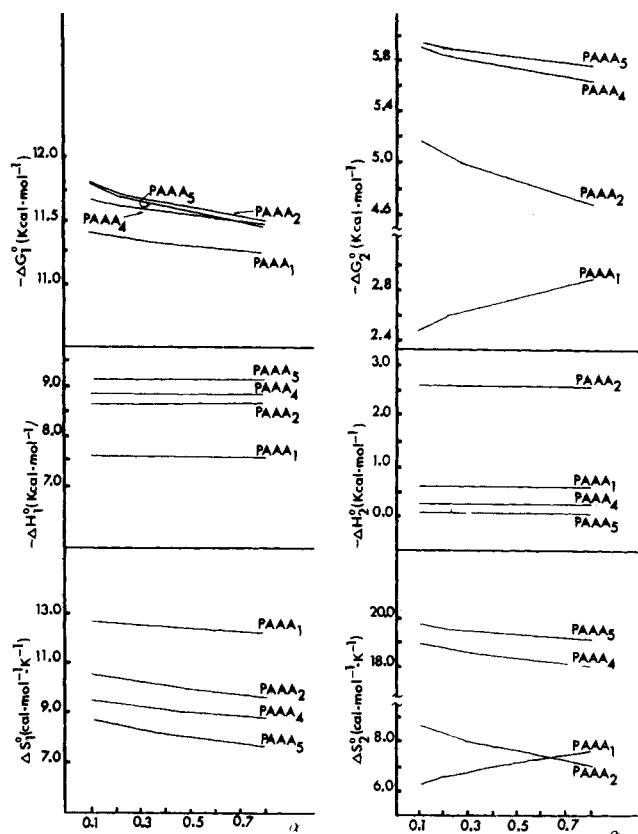


Figure 4. Dependence of the thermodynamic functions on the degree of protonation for polymer PAAA_n ($n = 1, 2, 4, 5$) at 25 °C in 0.1 M NaCl.

change increases, instead of decreasing, by increasing its protonation degree. This is probably related to the fact that the repeating unit of PAAA₁ assumes a compact conformation in its zwitterionic form, as already known in the case of simple α -amino acids¹⁷ with a partial internal neutralization of charges. Thus the protonation of the carboxylate group results in an opening of the structure. Since the overall positive charge on the macromolecular chain increases, the hydration shell of each unit increases on protonation. Then the cooperative effect between neighboring units determines an increase of liberation of water molecules as the protonation proceeds. In fact the protonation of a $\text{N}^+ \text{COO}^-$ unit with a near already protonated $\text{N}^+ \text{COOH}$ group provokes a larger loss of water solvent for the close presence of a more solvated group.

Conclusions

The spectroscopic data can be interpreted in terms of the mechanism of protonation without invoking any conformational transition with pH, which on the contrary occurs in some polymers.⁹⁻¹¹

The calorimetric results are particularly interesting because they show that the variation of the protonation constants with pH is due only to an entropy effect. The protonation enthalpies do not vary with pH, unlike in most typical polyelectrolytes.¹⁸ This behavior is similar to that observed in all poly(amido amines) studied so far in which, however, "real" protonation constants have been observed.¹⁹ Thus, the polymeric amido amino acids studied in this paper show an intermediate behavior between "classical" polyelectrolytes and the peculiar family of polyelectrolytes, poly(amido amines), for which the term "macroinorganic" has been proposed.^{20,21}

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Registry No. PAAA_n (*n* = 1), 99328-04-8; PAAA_n (*n* = 2), 99328-03-7; PAAA_n (*n* = 4), 99328-05-9; PAAA_n (*n* = 5), 99328-06-0; MAAA_n (*n* = 1), 99328-11-7; MAAA_n (*n* = 2), 99328-12-8.

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- (21) The poly(amido amines) look like small molecules for which the precise site of protonation and "sharp" basicity constants can be determined. Because of the similarity with some branches of "classical" inorganic chemistry, their studies are known as "macroinorganics".

Solution Crystallization of Poly(ether ether ketone)

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ABSTRACT: The morphology of spherulites and single crystals of poly(ether ether ketone) (PEEK) obtained from two organic solvents (α -chloronaphthalene and benzophenone) has been studied by electron microscopy and diffraction. Spherulites were found to consist of very narrow, elongated lamellar branches that grow with the *b* crystallographic axis in the radial direction. Single crystals possess a spearlike habit, with *b* parallel to the long axis, *a* transverse, and *c* (i.e., the molecular axis) normal to the lamellar plane. This habit becomes less anisometric with increasing growth temperature. Both single crystals and lamellae exhibit significant disorder and fragmentation, consisting of microcrystals whose widths (~ 15 – 22 nm) are only slightly larger than their thicknesses (~ 12 – 15 nm). Flow-induced crystallization on a planar substrate has also been studied and found to yield a morphology of fibrous-lamellar composites with preferential orientation of the *b* axis parallel (and of the *a* axis perpendicular) to the substrate. The morphological features of PEEK crystals grown quiescently or during flow have been interpreted in terms of molecular structure and chain packing.

Introduction

Poly(ether ether ketone) (PEEK) is the most common member of a new class of high-performance engineering thermoplastics, the poly(aryl ether ketones).¹ PEEK, whose repeat formula is $[-C_6H_4OC_6H_4OC_6H_4CO-]_n$ (with all linkages at the para position), has a melting temperature of ~ 335 °C and a glass-transition temperature of ~ 145 °C. Because of its high-temperature/high-strength characteristics and melt processability, PEEK is generating much interest for applications such as reinforced composites,^{2,3} coatings, electrical connectors, impeller housings, and many others.²

Molded specimens of PEEK have been examined by optical microscopy, differential scanning calorimetry, and X-ray techniques.⁴ X-ray diffraction on uniaxially oriented samples^{5,6} showed the unit cell to be orthorhombic ($a = 7.75$ Å, $b = 5.89$ Å, $c = 9.88$ Å) and very similar to those of other linear aromatic polymers, such as poly(*p*-phenylene oxide) [PPO]⁷ and poly(*p*-phenylene sulfide) [PPS].⁸ More recently, a tripling of the *c* axis length has been proposed⁹ to account for the chemical nature of the molecular repeat, although the chain conformation and packing have not been altered. X-ray diffraction and thermal techniques have also been used to study the effects of irradiation on molded PEEK sheets.¹⁰

One characteristic of PEEK that is of major importance in terms of performance, processability, and structural characterization is its exceptional chemical resistance.²

PEEK is described as insoluble in all common solvents² with the exception of strong acids (e.g., 98% sulfuric acid,¹ hydrofluoric acid,¹¹ or polyphosphoric acid¹²); solubilization in these acids is effected by protonation. Of these, 98% H₂SO₄ has been most widely used for molecular weight determinations by viscometric^{1,13} and light-scattering¹³ techniques. However, the latter study¹³ has shown that H₂SO₄ imparts significant chemical changes to PEEK as a result of extensive sulfonation. Therefore, strong acids are not appropriate for investigations of solution crystallization and morphology of PEEK, nor are they suitable for solution-processing techniques (e.g., casting or spin coating). Among other possible solvents mentioned in the literature,¹ the most effective have been found among the diaryl sulfones, although only at temperatures approaching the melting point of PEEK¹ (i.e., ~ 335 °C).

We have recently succeeded in dissolving PEEK in an organic solvent (α -chloronaphthalene) at much lower temperatures (~ 230 °C).¹⁴ From this solvent, ultrathin films were cast that could then be melted and recrystallized from either the molten or the quenched glassy phases. Their resulting structure and morphology, as revealed by electron microscopy and diffraction, have been reported elsewhere.¹⁵ Moreover, PEEK has also been crystallized from α -chloronaphthalene solutions in the form of single crystals,¹⁶ immature and mature spherulites, as well as flow-induced fibrous lamellar aggregates. Recently, we have extended our solution-crystallization studies to a