polymer reports

Macroinorganics IV: thermodynamic functions relative to the protonation of a poly(amido-amine) with repeating unit containing 3 amino groups

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(Received 17 April 1979)

Introduction

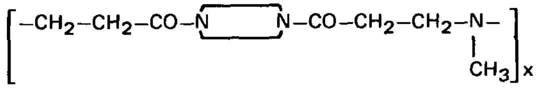
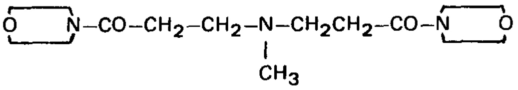
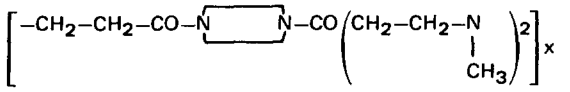
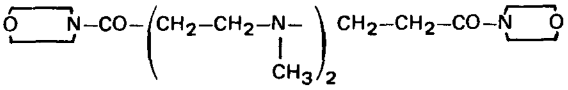
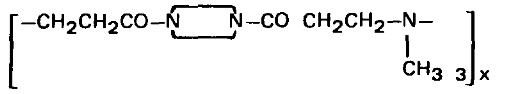
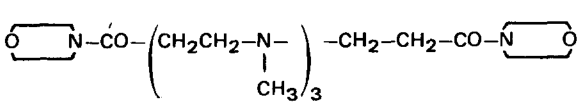
In the case of most polymeric acids and bases only 'apparent' constants can be determined [1]. However, we have found that poly(amido-amines), a new class of regular synthetic polymers resulting from the polyaddition of amines to bis-acrylamides, do not follow this rule. Indeed, 'real' basicity constants can be determined for these polymers in aqueous solution [2]. A calorimetric study on the protonation of poly(amido-amines), and their non-macromolecular models, having one or two basic nitrogens in the repeating unit, has been also performed [3].

In this report, we have investigated the thermodynamic functions relative to the protonation of a poly(amido-amine) (III) having three basic nitrogens in its repeating unit, and the corresponding model, in order to obtain a better knowledge of the protonation behaviour of this class of polymers in aqueous solution.

Results and discussion

The thermodynamic functions ΔG^0, ΔH^0 and ΔS^0 relative to the protonation of polymer III, and its model, are reported in *Table 1*. For purposes of comparison, the same

Table 1 Thermodynamic functions of protonation in 0.1 m NaCl at 25°C

Compound	Structure		$-\Delta G^\circ$ (cal mol^{-1})	$-\Delta H^{\circ a}$ (cal mol^{-1})	$\Delta S^{\circ a}$ (cal mol^{-1} deg^{-1})
Polymer I^b		$L + H^+$	10.62	8.26	7.9
Model I^b		$L + H^+$	11.00	8.41	8.7
Polymer II^b		$L + H^+$	11.03	7.35	12.3
		$LH^+ + H^+$	6.19	6.09	0.3
Model II^b		$L + H^+$	11.25	7.34	13.1
		$LH^+ + H^+$	6.55	6.05	1.7
Polymer III		$L + H^+$	11.02(3)	6.91(20)	13.8(7)
		$LH^+ + H^+$	9.46(7)	9.00(30)	1.6(1.0)
		$LH_2^{2+} + H^+$	2.58(48)	2.21(20)	1.4(2.0)
Model III		$L + H^+$	11.25(4)	6.33(20)	16.5(7)
		$LH^+ + H^+$	10.15(8)	9.30(20)	2.8(8)
		$LH_2 + H^+$	3.49(20)	2.90(23)	1.7(1.3)

[a] Values in parenthesis are the standard deviations

[b] Refs 2 and 3

0032-3861/79/101298-03$02.00

thermodynamic functions relative to some other poly (amido-amines), forming with III a homologous series with increasing numbers of basic nitrogens in the repeat units, are also reported in the Table.

All the protonation constants of polymer III are lower than those of its model. The corresponding ΔH^0 values are almost equal in the two compounds within the experimental errors. This may be also related to the close correspondence of their ^{13}C n.m.r. spectra [2]. The difference in the basicity constants is almost entirely due to the entropy terms. It may also be observed that the trend of the enthalpy and entropy values relative to the successive protonation steps for both polymer III and its model, is similar to that observed in linear aliphatic triamines [4]. The only notable feature is the large difference $|\Delta H_2 - \Delta H_1|$. In all previous cases this difference was considerably smaller ($\cong$ 0.8 cal mol^{-1}) and it was explained by a particularly favourable organization of the water molecules around the diprotonated triamine [4]. On the other hand, no enthalpy values of linear tertiary aliphatic triamine have been previously described. The overall trend of the ΔH^0 values may be conveniently explained by considering the different charges (Q_N) on the various nitrogen atoms for each protonation step. These charges have been calculated according to a method described previously [4]. In *Figure 1* we report the plot of ΔH_{exp} *versus* Q_N for all the studied poly(amido-amines). In spite of the crudeness of the method used, the correlation may be considered good. The only enthalpies not correctly accounted for are ΔH_2s of polymer III and model III.

In conclusion, even a poly(amido-amine) having three basic nitrogens in the repeating unit does not exhibit (in aqueous solution) typical polyelectrolyte behaviour towards protonation, as far as the basicity constants and protonation enthalpies are concerned. There is no difference, in this respect, between polymer III and the other poly(amido-amines) of this series. The substantial independence of the repeating units is possibly due to the presence of diacylpiperazine groups sheltering the positive charges on the protonated nitrogens present in different units.

Experimental

Materials

Poly(amido-amine) III, a sticky, non-crystalline material, was prepared as previously reported [2], and purified by dissolving in chloroform, reprecipitating with an excess of ether, and drying in high vacuum to constant weight; $[\eta]$ = 0.27 dl/g (in chloroform at 30°C).

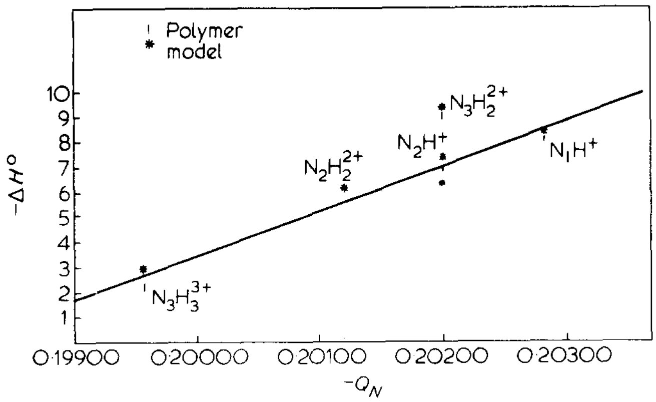


Figure 1 ΔH^0 (experimental) *versus* Q_N for poly(amido-amines) in the different protonation steps

Model III was prepared by allowing *N, N', N''*-trimethyldiethylentriamine to react with *N*-acryloylmorpholine in a 1 : 2 molar ratio in methanol solution. After standing for 4 days at room temperature, the reaction mixture was evaporated to dryness *in vacuo*. The oily residue was then purified by dissolving in benzene, reprecipitating with an excess of n-heptane, and drying in high vacuum. The product failed to crystallize. Yield, 85%. Analysis, found

Table 2 Experimental details of microcalorimetric measurements at 25°C in 0.1 M NaCl

Reaction	V_H^a (μmol s^{-1})	V_L^a (μmol s^{-1})	R^b (μl s^{-1})	Q^c (μcal s^{-1})
Polymer III + H^+				
	0.0423	0.0227	5.082	0.333
	0.0211	0.0227	3.383	0.156
	0.1061	0.0227	10.183	0.357
	0.0211	0.0453	5.073	0.148
	0.0423	0.0453	6.772	0.330
	0.0593	0.0453	6.772	0.429
	0.0593	0.0453	5.082	0.364
	0.1485	0.0227	10.183	0.373
	0.0295	0.0227	3.383	0.228
	0.0295	0.0453	5.073	0.213
	0.1485	0.0453	11.873	0.759
	0.2966	0.0231	10.183	0.401
	0.1183	0.0230	5.080	0.407
	0.0590	0.0230	3.383	0.381
	0.0590	0.0460	5.073	0.445
	0.2966	0.0460	11.873	0.787
	0.2966	0.0230	10.183	0.403
Model III + H^+				
	0.0394	0.0191	5.080	0.296
	0.0197	0.0191	3.383	0.139
	0.0394	0.0382	6.770	0.275
	0.0197	0.0382	5.073	0.133
	0.0197	0.0186	3.383	0.160
	0.0989	0.0186	10.183	0.432
	0.0399	0.0186	5.080	0.337
	0.3990	0.0186	10.183	0.402
	0.0793	0.0186	3.383	0.343
	0.2962	0.0186	10.183	0.346
	0.1181	0.0186	5.080	0.343
	0.0589	0.0186	3.383	0.321
	0.0589	0.0371	5.073	0.455
	0.1980	0.0186	10.183	0.340
	0.0789	0.0186	5.080	0.325
	0.0393	0.0186	3.383	0.308
	0.0393	0.0371	5.073	0.284
	0.0494	0.0225	10.183	0.340
	0.0197	0.0225	5.080	0.136
	0.0197	0.0449	6.770	0.132

Experimental details of the model III potentiometric measurements at 25°C in 0.1 m NaCl

Curve	Initial conc. (m x 10^3)	Range – log [H^+]	Number of points	Log *K*
A	2.349	9.1-2.5	50	8.253; 7.443; 2.564
B	1.665	8.7-2.6	44	
C	2.989	9.1-2.7	40	

[a] Total flow rates of the acid and compound

[b] Total flow rate

[c] Heat flow corrected for dilution

C 58.41%; H 9.82%; N 16.11% [$C_{21}H_{41}N_5O_4$ requires C 58.99%; H 9.67%; N 16.38%].

Methods

Potentiometric titrations were carried out using an Ag/AgCl reference electrode, an Orion 91–01 glass electrode and a salt bridge containing 0.1 m NaCl solution. For each determination the cell, thermostated at 25°C, was filled with ≅ 100 ml of 0.1 m Na Cl, containing a known amount of amine [2] The solution was titrated with 0.1 m hydrochloric acid solution, added through a Methrom Dosimat E 415 automatic piston burette under CO_2-free nitrogen.

The Miniquad 76 A program was used to calculate the equilibrium constants [5]

Calorimetric measurements were made with an LKB 10700-1 Flow calorimeter. The output voltages were rerecorded using a Keithley 153 Microvoltmeter.

The enthalpies of protonation were obtained using the continuous titration calorimetric method; the titrant (HCl) and the solution of the amine were introduced into the calorimeter at constant velocity by two Perfusor continuous infusion pumps. The enthalpy of formation of H_2O, obtained under the same experimental condition by mixing HCl with an excess of NaOH, was 13.34 cal mol^{-1}, in good agreement with the accepted value [6]

Numerical analysis of the data was handled by means of a previously described computer program [7].

Acknowledgements

We acknowledge partial support by Italian National Council of Research (CNR).

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