

hexagons was not observed for the copolymers. Destabilization of the  $\alpha$ -helix was not responsible for the enhanced tendency of the copolymers to form lamella crystals, since n.m.r. measurements showed that the poly(D,L-leucine) block had little or not effect on the stability of the PBLG  $\alpha$ -helix.

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## Protonation and complex formation of some novel poly(amido-amines)

Rolando Barbucci and Paolo Ferruti

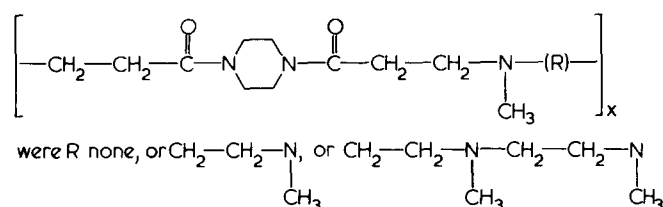
Sezione di Chimica Industriale e Inorganica Istituto Chimico, Via Mezzocannone, 4, 80134 Napoli, Italy

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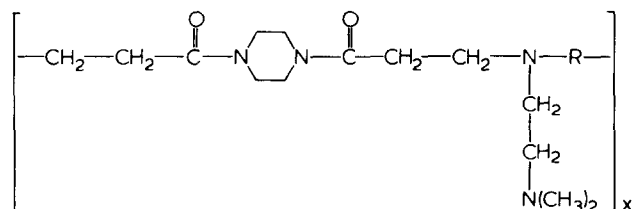
In previous research, we have found that tertiary amino polymers belonging to a new class, poly(amido-amines), show an unusual behaviour towards both protonation<sup>1-3</sup>, and complex formation with metal ions such as  $\text{Cu}^{2+}$ <sup>4</sup> and  $\text{Ni}^{2+}$ <sup>5</sup>.

In fact, 'real' basicity and stability constants could be determined in the case of poly(amido-amines). To our knowledge, no other polyelectrolytes showing this kind of behaviour have previously been described. In all previous cases, only 'apparent' constants were determined<sup>6</sup>.

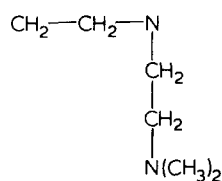
The poly(amido-amines) studied in our previous work had the following structure:



It may be noted that in all cases the tertiary amino groups were present as a part of the main chain. We thought it interesting to study the behaviour of poly(amido-amines) having a similar structure, but carrying additional amino groups as side substituents. Therefore, we synthesized the following new polymers:

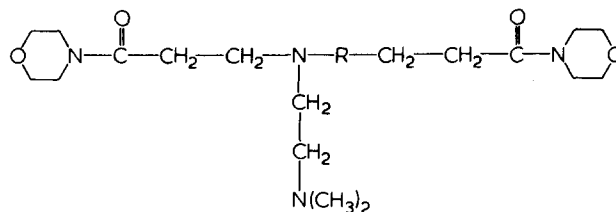


where R = none (polymer I), or



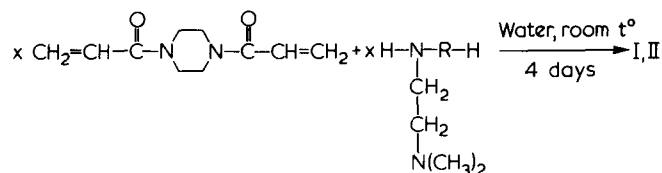
(polymer II).

We also, synthesized the corresponding non-macromolecular models:



where R has the same meaning as in the previous case.

The polymers were synthesized by polyaddition of 1,1-dimethylethylenediamine (I), or 1,1,10,10-tetramethyltriethylenetetramine (II), to 1,4-bisacryloylpiperazine, according to the following scheme:



The intrinsic viscosities of the polymers were 0.19 and 0.25 dl/g, respectively. They were measured in chloroform at 30°C. The C, H and N analyses gave satisfactory results.

The models were synthesized in a similar way, starting from the same amines, and N-acryloylmorpholine in a 1:2 molar ratio. They were viscous oils, and gave quite satisfactory analytical results.

The potentiometric titrations were performed as previously reported<sup>1,2</sup>. The results are summarized in Table I.

Table 1 Basicity and stability constants towards  $\text{Cu}^{2+}$  ion in 0.1 M NaCl at 25°C

Formula	Reaction	$\log K^a$
	$\text{L} + \text{H}^+$	LH 8.87 (1)
	$\text{LH}^+ + \text{H}^+$	$\text{LH}_2^{2+}$ 4.10 (2)
	$\text{L} + \text{Cu}^{2+}$	$\text{CuL}$ 8.47 (5)
	$\text{L} + \text{H}^+$	$\text{LH}^+$ 9.02 (2)
	$\text{LH}^+ + \text{H}^+$	$\text{LH}_2^{2+}$ 7.91 (4)
	$\text{LH}_2 + \text{H}^+$	$\text{LH}_3^{3+}$ 4.47 (8)
	$\text{LH}_3^{3+} + \text{H}^+$	$\text{LH}_4^{4+}$ 2.15 (22)
	$\text{L} + \text{Cu}^{2+}$	$\text{CuL}$ 16.05 (18)
	$\text{L} + \text{H}^+$	$\text{LH}^+$ 9.05 (1)
	$\text{LH}^+ + \text{H}^+$	$\text{LH}_2^{2+}$ 4.35 (2)
	$\text{L} + \text{H}^+$	$\text{LH}^+$ 9.05 (1)
	$\text{LH} + \text{H}^+$	$\text{LH}_2^{2+}$ 8.34 (2)
	$\text{LH}_2^{2+} + \text{H}^+$	$\text{LH}_3^{3+}$ 4.42 (4)
	$\text{LH}_3^{3+} + \text{H}^+$	$\text{LH}_4^{4+}$ 2.42 (8)

<sup>a</sup> The values in parentheses are the standard deviations

All the basicity constants are 'real', as in all the previously studied poly(amido-amines). It may also be observed that there is a close correspondence between the polymers and their non-macromolecular models. The stability constants determined with  $\text{Cu}^{2+}$  ion are also 'real' and from a comparison with our previous results<sup>4,5</sup>, they suggest that a full coordination by all the tertiary amino groups present in the repeating unit takes place<sup>7</sup>. It follows that the position of the tertiary amino groups, either in the main chain, or in the side substituents, is irrelevant, as far as the protonation and complex formation behaviour are concerned.

Having been ruled out a possible influence by the position of the tertiary amino groups, the unusual behaviour of poly(amido-amines) might be explained by the presence in the macromolecular chain of ring structures, namely 1,4-diacyl piperazine groups, shielding the tertiary amino groups of a given unit from the rest of the macromolecule. Possibly, too, the distance between the tertiary amino groups along the macromolecular chain is itself sufficient to avoid interactions between different units. In order to elucidate this point,

we are now synthesizing some poly(amido-amides) in which the distance between the tertiary amino groups is the same as in the previous cases, but no ring structures are present along the macromolecular chain.

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