

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY
in conjunction with the
GESELLSCHAFT DEUTSCHER CHEMIKER

XXIVth INTERNATIONAL
CONGRESS OF PURE AND
APPLIED CHEMISTRY

VOLUME 1

*Plenary and main section lectures presented
at Hamburg, Federal Republic of Germany,
2-8 September 1973*

LONDON
BUTTERWORTHS

UNION INTERNATIONALE DE
CHIMIE PURE ET APPLIQUEE
en relation avec la
GESELLSCHAFT DEUTSCHER CHEMIKER

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PURE ET APPLIQUEE

TOME 1

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présentées à Hambourg, République
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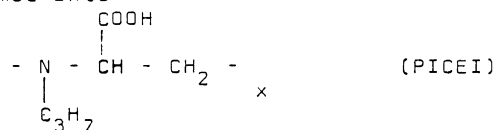
SOME NEW POLYMERS, THEIR SYNTHESSES AND PROPERTIES

G.J. SMETS

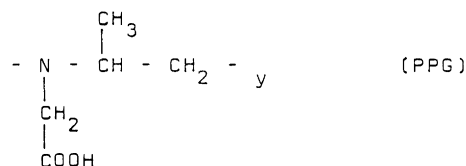
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Louvain, Belgium

ABSTRACT

The synthesis of polyampholytes with small repeat unit has been achieved by cationic ring opening polymerization of N-substituted carboxymethyl aziridines, followed by alkaline hydrolysis of the polyamino carboxylic acid ester. Using this two-step method, N-isopropyl-2-carboxymethyl-aziridine has been transformed into



Similarly optically active L- and racemic N-propyleneglycine give

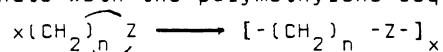


The two acid dissociation constants of these poly- α -amino-carbonic acids have been determined on the basis of the Henderson Hasselbach equation, as modified by Katchalsky and Spitnik. Their complexation properties towards bivalent metal ions were also determined using the classical Bjerrum method; the diagrams indicated a limited value of two repeat-unit per metal ion. The complex formation constants are equivalent for racemic and L-PPG; they are appreciably higher for PPG than for PICEI, and are compared with the complex formation constants of their low molecular weight homologues. The equilibrium ion-binding capacities of cross-linked PPG depend strongly on the nature of the metal and on the pH of the solution.

In the second part of the lecture, the syntheses of unsubstituted and substituted N-vinyl-vic.triazoles are described on the basis of the dipolar cycloaddition of alkyl/aryl azides with unsaturated compounds. Similarly, vinyl tetrazolinones were obtained by cycloaddition of azides to aromatic isocyanates and arylsulfonisocyanates. The polymerization behavior as well as some characteristic properties of these derivatives are further considered.

INTRODUCTION

During the last decade several researches have been devoted to the study of the ring-opening polymerization of ring compounds containing one or more heteroatoms. Much progress has been achieved in our knowledges about their reaction mechanism; the relationship between ring size and polymerizability is undoubtedly one of the most fundamental problems in this domain. From the organic point of view ring-opening polymerization offers the possibility to prepare regular polymers with predetermined sequence length, depending on the number n of ring-carbon-atoms, in which the heteroatom Z will alternate with the polymethylene sequence.



This polymerization principle has been applied to the synthesis of some new polyampholytes, based on the ring-opening polymerization of aziridine derivatives, and on which properties we will report in the first part of this lecture.

On the other hand, cycloaddition reactions have been largely investigated during the last years in order to synthesize single strand and ladder polymers; some of these syntheses were recently reviewed by Stille (1). Cycloaddition permits however also to synthesize easily new vinyl derivatives containing three and four hetero-atoms into their ring. Scarce are the data of the litterature concerning their syntheses, their polymerization behavior and the influence of the accumulation of heteroatoms on their reactivities. Therefore in the second part of this lecture, we will report about recent results concerning new triazoles and tetrazolinones, and describe some of their characteristic properties.

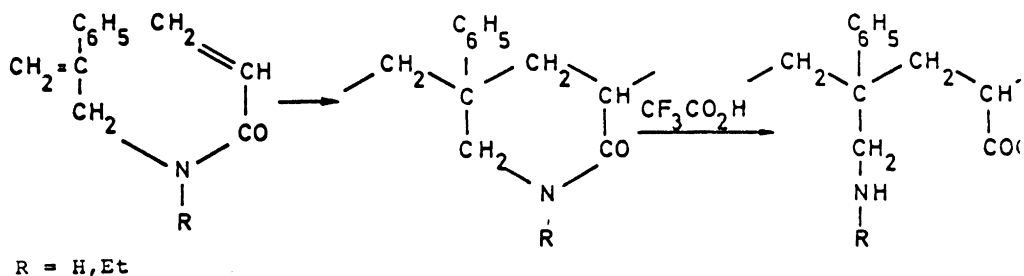
I SYNTHETIC POLYAMPHOLYTES

(with collaboration of Dr. J. Vande Putte and Dr. C. Samyn)

It is well known that the synthesis of polymeric ampholytes can easily be carried out by direct copolymerization of an acidic and a basic vinyl monomer, e.g. acrylic acid and vinylpyridine. These copolymers present however a great disadvantage : their internal structure is only known on a statistical basis, resulting from the corresponding copolymerization parameters. In our knowledge the monomer sequences distribution e.g. triades as determined by nuclear magnetic resonance has not been described up to now. On the other hand their constitution ampholyte base-unit has a relatively high molecular weight, which causes a low solubility or precipitation in the region of the isoelectric point. Similar objections are also applicable to copolymers resulting from chemical modification of preexisting polymers : the influence of the neighboring group, functional interaction, variation of charge distribution in the course of reaction and increased steric hindrance are often responsible for limited degrees of conversion and "secondary" effects which make the internal structure even more undefined. It seemed therefore necessary to consider another approach to the problem, if one desires to obtain high molecular weight polyampholytes with alternating structures.

Different attempts have been described recently in the literature, and will be shortly reviewed.

Panzik and Mulvaney used the principle of the cyclopolymerization of N-2-phenylallylacrylamide, where both unsaturated units are linked by an hydrolyzable amide group. (2)



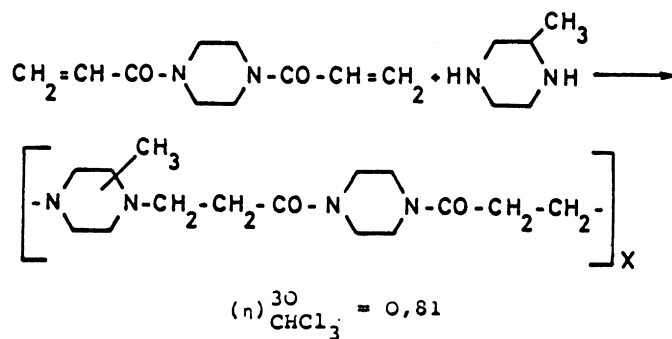
Using a radical initiator or a Lewis acid (ZnCl_2 , EtAlCl_2 - EtAlCl_2) a cyclopolymer was obtained; on hydrolysis a polyampholyte is obtained of which the solubility is much higher than that of the precursor polymer.

Two main difficulties still exist in this approach :

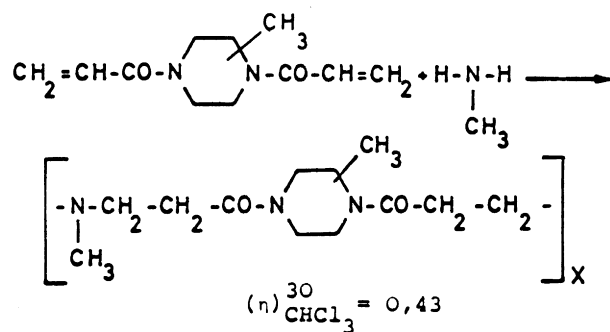
- i) complete cyclopolymerization is difficult to achieve.
- ii) the hydrolysis succeeds only partially.

Consequently the final aim of obtaining polymers with complete regular structure is only partially fulfilled.

Another reaction principle, described by Denusso and Ferrutti is based on a polyaddition technique, that these authors did use for the synthesis of water soluble polyampholytes. (3) In this method bifunctional unsaturated base units, activated with α -carbonyl or α -sulphonyl groups are condensed with bis-secondary amines, e.g. between 1,4. diacrylylpiperazine and methylpiperazine.



or with a primary amine :



With glycine (or β -alanine), in the presence of a volatile tertiary amine, one obtains with 1.4. acrylylpiperazine :

