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New Polyimidazolyl and Pyrazolyl Esters

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Dedicated to the 60th anniversary of Prof. C.I. Simionescu

SUMMARY

New polyimidazolyl and polypyrazolyl esters were synthesized by polycondensation of the chlorides of the pyrazolyl and imidazolyl dicarboxylic acids with ethylene glycol,pentamethylene glycol and glycerol.

INTRODUCTION

Recent studies on the correlation between the properties and the chemical structure of the polymers containing imidazolic heterocycle have confirmed their catalytical enzyme-like properties.In the field of macromolecular compounds simple structural analogies were achieved by means of homo and copolymers and of condensation products modified with azoles.Enzymatic models analogous to the natural ones were thus performed (KUNITAKE 1972,DAVIES 1973,FERSHT 1970,OVERBERGER 1970, 1974).The present paper is concerned with obtaining of imidazolic and pyrazolic monomers able to lead further with dihydroxy- and trihydroxyalcohols to polycondensation products for synthesizing then polyimidazol and polypyrazol esters.

EXPERIMENTAL

4,5-Imidazolyldicarboxylic acid. 7 g (0.06mole) benzimidazole are solved in 61.7 ml of 70% H_2SO_4.53 g $K_2Cr_2O_7$ are then added in portions,under stirring,maintaining the temperature between 70-80°.The oxydation duration is of 4 h.After removing the inorganic salts by washing repeatedly with water the product is obtained in 28% yield.The 4,5-imidazolyldicarboxylic acid is a white powder which decomposes at about 288°.
3,5-Pyrazolyldicarboxylic acid. 5 g (0.052 mole) of 3,5-dimethylpyrazol are solved in 200 ml of water and oxydized with $KMnO_4$ (35 g) on a water bath for 3 h.The mineral oxides are filtered and the solution evaporated under vacuum till 80 ml and treated then with 10 ml of acetic acid.The crystalline kalium imidazolate thus obtained is passed into the dicarboxylic acid by treating with 60 ml of N/2 HCl.The product is obtained in a 60% yield.Melting point: 290° with decomposition.
The dichlorides of imidazolyl and pyrazolyldicarboxy-

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lic acids are obtained by refluxing 3.5 g (0.0022 mole) dicarboxylic acid, 18.5 g of SO_2Cl_2 and 1.2 ml of DMF, for 3 h. The unreacted SO_2Cl_2 is evaporated under vacuum and DMF distillated with 20 ml methylene chloride. Are thus obtained: the dichloride of the 4,5-imidazolyldicarboxylic acid as a white-yellow product, decomposing at 320°, yield: 80%, the dichloride of 3,5-pyrazolyldicarboxylic acid as a solid white product, decomposing at 324°, yield: 88%.

The polycondensation was carried out by the interfacial method in the water-benzene system.

RESULTS AND DISCUSSION

The imidazolic monomer was prepared by the oxidation of benzimidazole followed by its conversion into acide chloride. The literature method for benzimidazole oxidation by kallium permanganate (BAMBERGER 1893) failed in giving good results. By oxidation with sodium bichromate (VINOGRADOVA 1965) the 4,5-imidazolyldicarboxylic acid was obtained. The method was applied for the synthesis of the imidazolyldicarboxylic acid chloride by employing the thionyl chloride and dimethylformamide as catalyst (BOSSHARD 1959) instead of phosphorus pentachloride (HOFFMANN 1975). This method is advantageous because of a higher reaction rate and yield and a facile separation of the acid chloride from the reaction medium.

For preparing the pyrazolyl dichloride, the 3,5-pyrazolyldicarboxylic acid was synthesized by oxidation 3,5-dimethylpyrazol (KNORR 1894) obtained in its turn from acethylacetone and hydrazine sulphate (WILEY 1951).

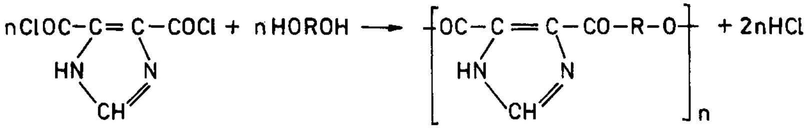
The structure of the heterodicarboxylic acids and their conversion into chlorides were followed by analytical and spectral methods (Table 1).

TABLE 1

Compound	m.p. (°C)	C (%)	H (%)	N (%)	i.r. $\nu_{C=O}$ (cm^{-1})
4,5-Imidazolyldicarboxylic acid	323	38.02	2.63	17.79	1680
4,5-Imidazolyldichloride	188	30.78	1.10	15.21	1770
3,5-Pyrazolyldicarboxylic acid	290	37.94	3.33	17.46	1710
3,5-Pyrazolyldichloride	326	30.62	1.14	15.30	1770

The strong electronegative chlorine atom causes a positive charge on the carbon in C=O group, the carbonylic structure being hence favoured rather the polar one. The frequency of the C=O group becomes thus specific occuring at higher values.

For syntheses of polyesters the chloride of dicarboxylic pyrazolyl and imidazolyl acids,ethylene glycol and pentamethylene glycol as dihydroxyalcohols and glycerol as trihydroxyalcohols were employed.



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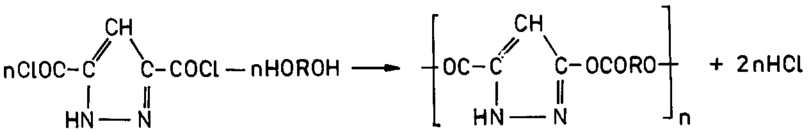

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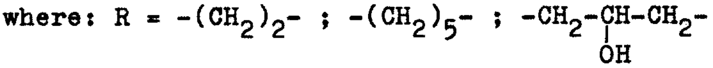
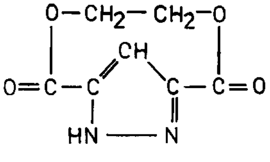


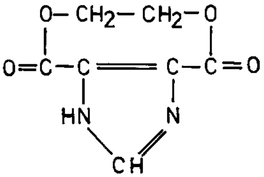
where: R = $-(CH_2)_2-$; $-(CH_2)_5-$; $-CH_2-\underset{OH}{CH}-CH_2-$

The polycondensation was carried out by the interfacial method in the water-benzene system.The glycerol was chosen as polycondensation component to introduce hydroxyl groups on the macromolecular chain.These groups together with the imidazolic ring will participate to formation of the active center catalysing the hydrolisis reaction,similar to that existing in the enzymes.

Poly(ethylene glycol 3,5-pyrazol dicarboxylate) and poly(ethylene glycol 4,5-imidazol dicarboxylate) are synthesized starting from the acid chlorides and ethylene glycol taken in equimolar ratios.The IR spectra of the polymers (Fig.1,curves a and b) show absorption bands characteristic of the esteric groups (ν C=O 1690 cm^{-1}) as well as two bands characteristic of the cyclic esters (1730 and 1890 cm^{-1}) of the structures III and IV.



III



IV

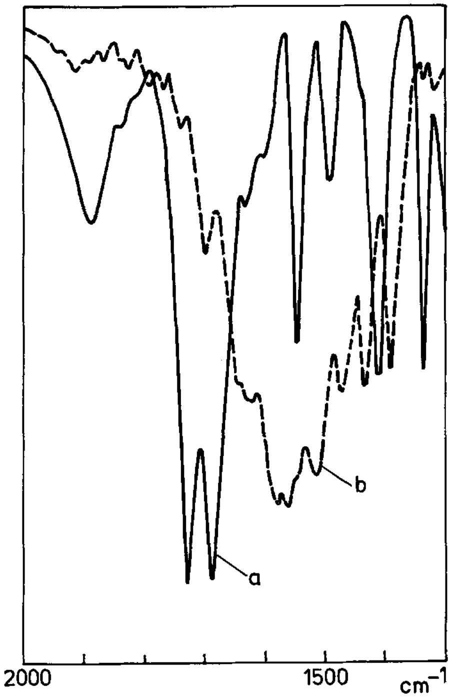


Fig.1 Infra-red absorption of poly (ethylene glycol 3,5-pyrazol dicarboxylate)(curve a̲) and poly(ethylene glycol 4,5-imidazol dicarboxylate)(curve b̲)

After extraction in DMF the products do not show the absorptions characteristic of cyclic esters which indicates that the cyclization did not take place at the ends of the macromolecular chains.The cyclic ester content in poly(ethylene glycol 3,5-pyrazol dicarboxylate) is much higher (0.75%) than in poly(ethylene glycol 4,5-imidazol dicarboxylate)(0.08%).Nine membered ring formed from the chloride of the dicarboxylic pyrazolyl acid and ethylene glycole is more stable than formed from the chloride of the dicarboxylic imidazolyl acid.The formation probability of cycles with pyrazol residue is increased when the chloroanhydride groups are located in the c̲i̲s̲ position towards the ring.The eight membered cyclic esters formed with the chloride of the dicarboxylic imidazolyl acid might be regarded as seven membered rings from the stability point of view since the rigid double bond may be considerred as a single term.The less stable seven membered rings show the tendency of passing into linear polymers which accounts for some quantitative differences.By employing pentamethylene glycol as polycondensation component only linear polymers were obtained. Glycerol leads to linear polymers with free hydroxyl groups.By applying the method based on phtalic anhydride in pyridine medium the value of 4.65% was found for the OH content.The polymers were obtained as white powders. Their intrinsic viscosities measured in concentrated sulphuric acid at 35° are given in table 2.

TABLE 2

Polymer	$[\eta]$ (dl/g)
Poly(pentamethylene glycol 4,5-imidazol dicarboxylate)	0.132
Poly(pentamethylene glycol 3,5-pyrazol dicarboxylate)	0.100
Poly(glycerol 4,5-imidazol dicarboxylate)	0.052

By carrying out the polycondensations under the same conditions a rather reduced difference between the reactivities of the acid chlorides was noticed; the obtained polymers showed closed intrinsic viscosities having hence molecular weights almost equal. Glycerol showed a different behaviour leading to polymers of low molecular weight.
The synthesized polymers are partially soluble in hot pyridine, DMF, N-methyl pyrolidone and soluble in concentrated sulphuric acid and show a good thermal stability. The chain destruction begins at 330° when an exothermal process is noticed with weight losses of 82%. At 153° and 290° less significant destructions occur attributable to the decarboxylation of the end groups and to the dehydration of the hydroxyl groups.

CONCLUSIONS

The acid chlorides of imidazolyl and pyrazolyl dicarboxylic acids were synthesized by employing the thyonyl chloride and DMF in catalytic amounts. The polyesters were prepared by the reaction of the chlorides of diazolyldicarboxylic acids with ethylene glycol, pentamethylene glycol and glycerol in equimolar ratios. In the structure of poly(ethylene glycol 3,5-pyrazol dicarboxylate) and poly(ethylene glycol 4,5-imidazol dicarboxylate) the micromolecular cyclic esters were found. With pentamethylene glycol and glycerol as polycondensation components only linear polymers were obtained. Poly(glycerol diazolates) have a free hydroxyl group content of 4.65%. The synthesized polyesters are soluble in strong acids and partially soluble in some solvents such as DMF, N-methyl pyrolidone and show a good thermostability.

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