

## New Monomers and Polymers. V.\* Study of the Spontaneous Polymerization of 5-Ethoxycarbonyl-3-formyl-2-pyrazoline

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### Synopsis

The 3-formyl-2-pyrazolines (pyrazoline-3-carboxaldehyde) obtained by 1-3 dipolar additions of diazoesters to acrolein are unstable and smoothly polymerize through the aldehyde group to a polyacetal polymer. On the basis of spectroscopic data, this paper describes the structure of the isolated polymers, along with their properties and a polymerization mechanism. It is proposed that a nucleophilic attack of a heterocyclic amino nitrogen on another monomer formyl group leads to an internal ion pair, and that this latter promotes a polycondensation of other aldehydic units according to an anionic type of propagation. The results are polyacetal polymers of low molecular weight with conservation of the heterocyclic framework. However, numerous side reactions are possible and account for the relatively low molecular weights observed.

### INTRODUCTION

Cycloaddition reactions of diazo compounds to  $\alpha,\beta$ -unsaturated aldehydes have been known for a long time to afford polymeric materials.<sup>2,3</sup> However, the structure of those polymers has never been elucidated.

We have previously observed<sup>4</sup> that 3-formyl-2-pyrazoline (I) (pyrazoline-3-carboxaldehyde) resulting from a 1-3 dipolar addition of ethyl diazoacetate (EDA) to acrolein is unstable and rapidly polymerizes. The purpose of this paper is to describe the polymerization of the intermediate pyrazoline (I) and the structure and properties of the polymers obtained and to propose a mechanism for the polymerization itself.

### EXPERIMENTAL

#### Reagents

All the polymerizations were performed in benzene previously distilled from lithium aluminum hydride under an inert atmosphere. The reactants, acrolein and ethyl diazoacetate, were distilled before reaction.

\* For the previous paper in this series, see Teyssié and Korn-Girard.<sup>1</sup>

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### Polymerization

Some control reactions were conducted under a nitrogen atmosphere, but no major difference was observed when no such precautions were overtaken.

The experiments were performed with initial concentrations of acrolein of 0.5, 1 and 5M at 30, 50, and 78°C with a molar ratio of EDA to acrolein of 1 or 1.2.

Into a previously dried 250-ml, three-necked flask equipped with a magnetic bar, a reflux condenser, and a nitrogen bubbler was placed 6.65 ml of acrolein in 81.5 ml of benzene. Then, 10.5 ml of ethyl diazoacetate, previously thermostatted at 25°C, was quickly added, affording a solution 1M in each reactant. The solution was stirred and raised to the desired temperature. After 6 days, the reaction mixture was poured into 800 ml of hexane, and the solid that formed was filtered, washed with hexane, and dissolved in 100 ml of chloroform, to be precipitated again twice in hexane. The off-yellow solid obtained weighed 13.7 g (80% yield) and decomposed at 120°C.

ANAL. Calcd for  $(C_7H_{10}N_2O_3)_n$ : C, 49.41%; H, 5.88%; N, 16.47%. Found: C, 49.3%; H, 5.8%; N, 16.6%.

### Measurements

Infrared spectra (KBr pellets or in chloroform solution) were recorded on a Perkin-Elmer 21 spectrometer, and  $^{13}C$ -NMR spectra on a Bruker HFX-90 apparatus at 22.63 MHz (chemical shifts in ppm, downfield from TMS). Gel-permeation chromatograms were recorded at 25°C from tetrahydrofuran solutions (15 mg/10 ml), on a Water Associates instrument with four Styragel columns of  $10^7$ ,  $3 \times 10^5$  and  $3 \times 10^3$  Å porosities. The number-average molecular weights  $\bar{M}_n$  of the polymers were determined by osmometry in chloroform solution by using a Knauer vapor-pressure osmometer.

### RESULTS

The stoichiometric addition of the reactants to give the polymer without any loss of nitrogen is established on the basis of the elemental analysis of all the polymeric fractions. The polymers are thermally stable up to 120°C.

The main observation is that in all the experiments, molecular weights, as determined by osmometry  $\bar{M}_n$ , and the polydispersity of the polymer as analyzed by GPC, are directly proportional to the reaction times, temperatures, and concentrations (Table I).

However, polymerization is subject to some limitations: a temperature higher than 50°C affords a polymer of lower molecular weight, while performed at room temperature, without any solvent, the reaction becomes extremely violent.

The molecular weight of the polymer reaches a maximum value of 3200 and does not increase further even after 2 weeks at 25°C. Those values correspond to a mean degree of polymerization of about 20 units. No higher molecular weights are obtained with highly purified reactants.\*

\* However, as a referee pointed out, simple distillation does not eliminate the ethyl glycinate which contaminate, commercial EDA, and the latter is perhaps an impurity limiting molecular weights.

TABLE I  
Experimental Conditions and Properties of the Polymers  
Obtained by Addition of Ethyl Diazoacetate to Acrolein in Benzene

Polymer	Acrolein concn, mole/l. <sup>a</sup>	T°,C	Reaction time, days	$\bar{M}_n$	Polymer yield, %	dn/dc cc/g
1	1	25	1	700	60	0.1438
2	1	25	2	1100	70	0.1418
3	1	25	3	1200	73	
4	1	25	6	1700	80	0.1270
5	1	25	8	2800	84	
6	1	25	13	3200	88	0.1169
7	0.5	30	5	1600	81	
8	1	30	5	1600	85	
9	5	30	5	2750	92	
10	0.5	50	5	1800	87	
11a <sup>b</sup>	1	50	5	2000	60	0.1270
b				2600	29	
12a <sup>b</sup>	5	50	5	1500	35	
b				3000	59	

<sup>a</sup> Polymerizations at 25°C with a molar ratio of EDA/acrolein = 1; at 30°C and 50°C, EDA/acrolein = 1.2.

<sup>b</sup> Reactions yielding some benzene-insoluble fractions: 11b and 12b are soluble in chloroform; 11a and 12a are soluble in benzene, chloroform, and tetrahydrofuran.

Since no reference is available, it is not possible to calculate the polydispersity  $\bar{M}_w/\bar{M}_n$  which is probably high; nevertheless, the almost symmetrical distribution of molecular weights is evidence supporting a one-pathway polymerization mechanism.

Differential refractometry shows large variations of the refractive index gradient  $dn/dc$  decreasing with the  $\bar{M}_n$  enhancement (Table I). This finding argues for a continuous change in the relative distribution of terminal and internal functional groups on the growing polymer chain.

### Structural Study

The infrared spectra obtained from samples prepared at different temperatures and reaction times reveal important differences in the absorption intensities. These modifications, which are always directly related to the  $\bar{M}_n$ , are shown in Figure 1 and compared with the monomer spectrum.

The intensities of the absorptions at 1735 and 1185  $cm^{-1}$  remain constant in all the samples and characterize unconjugated ester groups which thus appear unmodified over the entire polymerization process. On the contrary, the decreasing intensities of both the aldehydic CH stretching vibration (2860  $cm^{-1}$ ) and especially of its carbonyl vibration (1665  $cm^{-1}$ ) indicate a progressive disappearance of the formyl group. A similar evolution is observed for the conjugated azomethine (1550  $cm^{-1}$ ).<sup>5</sup> Together with the decrease of both conjugated aldehyde and azomethine functions, a new absorption which is attributed<sup>6</sup> to a nonconjugated C=N appears at 1610  $cm^{-1}$ .

The loss of conjugation of this latter bond therefore suggests a progressive

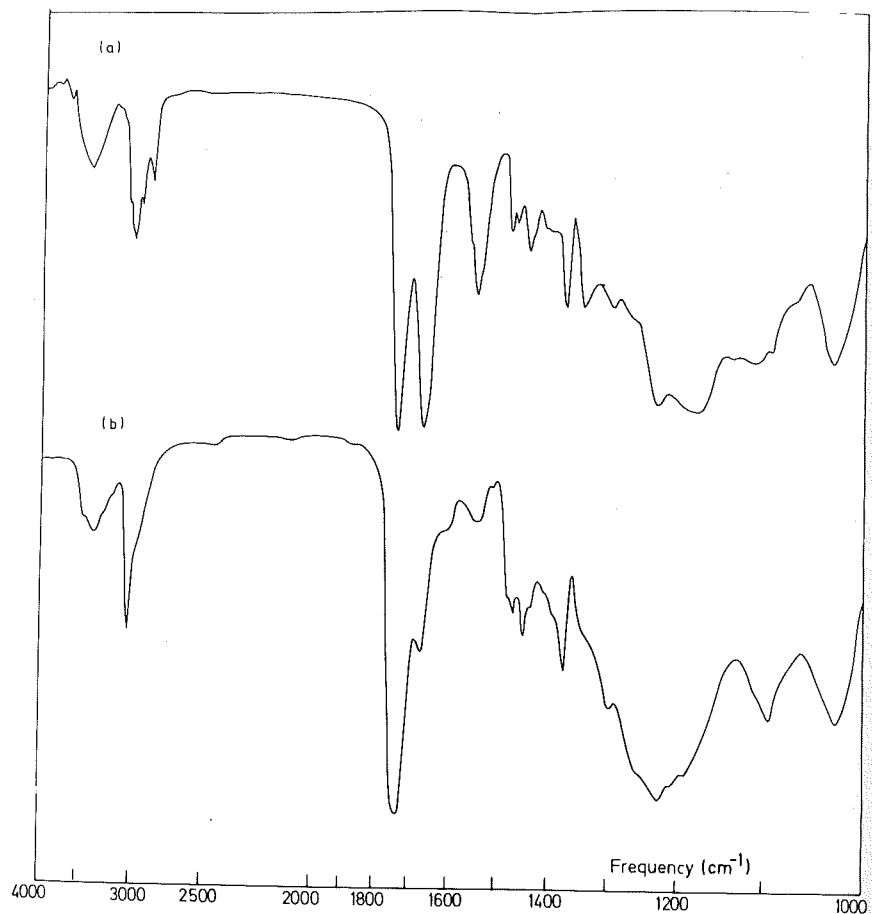
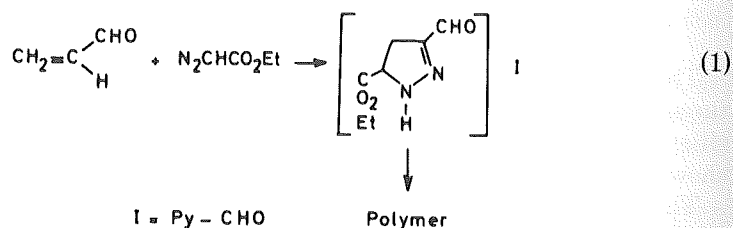
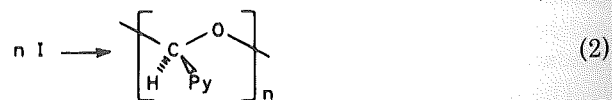


Fig. 1. Infrared spectra of: (a) monomeric 5-ethoxycarbonyl-3-formyl-2-pyrazoline; (b) polymeric 5-ethoxycarbonyl-3-formyl-2-pyrazoline.

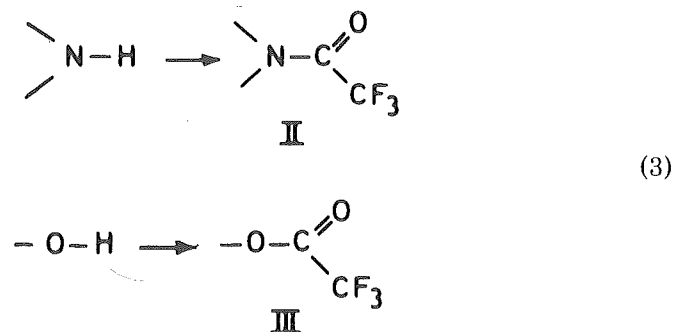
disappearance of the formyl groups related to the increase of polymerization degree and due to its participation to the polymerization scheme:



In addition, the intensity of a new strong absorption band around  $1220 \text{ cm}^{-1}$  is directly proportional to the disappearance of formyl groups.<sup>7</sup> This absorption, which is quite broad and partially masks the ester valence vibration, is assigned to a polyacetal system [eq. (2)]. This large band is also seen in the spectrum of the polymer obtained from acrolein and diazomethane ( $1220\text{--}1200 \text{ cm}^{-1}$ ).



The presence of polyacetal bonds in these oligomers is further supported by NH determinations: the amino hydrogen content remains high with respect to the formyl and hydroxyl contents as shown by the acetylation experiments. Those latter were performed with trifluoroacetic anhydride to achieve resolution of the broad absorption between  $3450$  and  $3300 \text{ cm}^{-1}$ . In this way, separation of NH and OH functions is straightforward: two new absorptions which correspond to II and III<sup>8</sup> show up at respectively  $1695$  and  $1790 \text{ cm}^{-1}$  [eq. (3)].



Although the absorption coefficients  $\epsilon_{\text{CO}}$  of these two vibrations have not been measured, the ratio of their intensities clearly shows a number of NH groups much higher than the OH ones. This result is in agreement not only with the conservation of the NH function during the reaction but, together with the presence of an azomethine  $\text{C}=\text{N}$ , with the conservation of the heterocyclic structure and a polymerization through the aldehyde group to a polyacetal polymer.

<sup>13</sup>C-NMR spectra of the polymer show absorptions at 98.5, 96.4, and 93.8 ppm downfield from TMS, which are tentatively assigned to the acetal carbons, while an absorption at 81.17 ppm is assigned to an hemiaminal or an aминаl termination. The residual formyl group shows up at 182.3 ppm.

## DISCUSSION AND MECHANISM

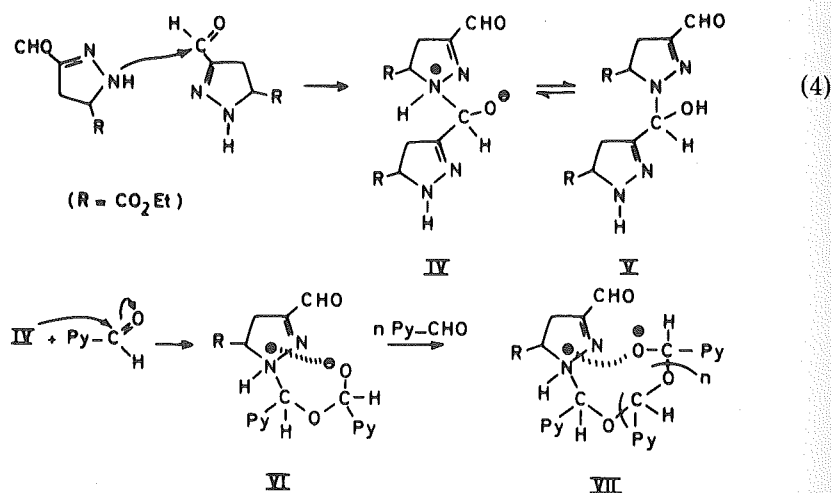
The formation of a polyacetal system by condensation of aldehyde units is an important feature of the polymerization mechanism of 3-formyl-2-pyrazolines.

Polymerizations of aldehydes (formaldehyde,<sup>9</sup> acetaldehyde, acrolein,<sup>10,11</sup> 2-formyl-5-dihydropyran<sup>12</sup>) have already been studied. However, the uncatalyzed polymerization of 5-carboethoxy-3-formyl-2-pyrazoline I remains quite unusual.

It was previously found that the *N*-acetyl derivative of I as well as the 1,5-diphenyl-3-formyl-2-pyrazoline are stable towards polymerization.<sup>13</sup> Thus the loss of nucleophilicity, and eventually some additional steric hindrance of the monomer are sufficient to prevent any polymerization. In the same way, the molecule is stable and does not polymerize if the formyl function is replaced by an acetyl group.

It seems obvious that the nucleophilic nitrogen of the heterocycle reacts with the electrophilic carbonyl formyl group of a second molecule (either as 2-pyrazoline or as a presumably more electrophilic 1-pyrazoline). This first step

generates an internal ion pair IV [eq. (4)] which then induces the polymerization of other formyl groups, according to an anionic type of propagation. This mechanism is also supported by the fact that 2-formylpyrroles<sup>14</sup> with a less basic nitrogen are quite stable and do not dimerize or polymerize.

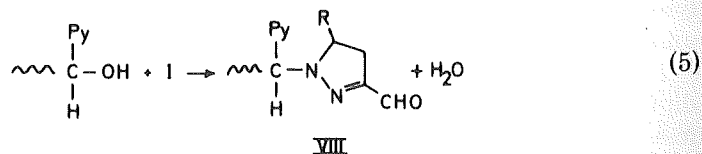


This mechanism, with regular insertion of monomers between the ionic centers of the growing chain, avoids a large separation of the charged species and, together with numerous side reactions (see below), could explain the fact that only low molecular weight polymers are obtained.

An alternative process can also be visualized by considering the interaction of two or more initiator molecules IV in a cyclized or paired system<sup>15</sup> and subsequent insertion of monomers leading to the simultaneous formation of several polymeric chains. This second propagation pathway could, however, be disfavored by entropy considerations.

Termination can be achieved through recombination of an anion with a proton of a quaternary nitrogen and formation of hemiaminals V; the hydroxyl groups observed in the infrared spectra are probably the result of the formation of such hemiaminal functions.

On the other hand, polyacetal systems with hemiacetal end groups are usually known for their tendency to depolymerize. Since no such effect is observed in this case (GPC, tonometry), it is probable that a subsequent formation of a more stable aminal function VIII [eq. (6)] can occur to some extent.



A condensation of an aldehyde group with a basic NH function has already been observed in the dimerization of ester derivatives of 5-formyl-5-methyl-2-pyrazolines.<sup>16</sup> However, hemiaminals of this type have been shown to be surprisingly stable, and the formation of such a function could be a termination in itself.

## CONCLUSIONS

The proposed mechanism, with a propagation step involving polyaddition of formyl functions and promoted by a condensation of two monomeric pyrazolines, is in good agreement with the spectral data discussed above. Moreover, the enhancement of the polydispersity, the variations of the ratio of the different functions carried by the monomer and the moderate chain lengths observed during the polymerization are also well accounted for by the formation of a highly strained polyacetal and the complexity of secondary reactions possible.

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