THE HETEROCYCLIZATION OF SOME REACTIVE POLYMERS BY A 3 + 2 DIPOLAR CYCLO-ADDITION REACTION—II

POLYAMIDES AND POLYHYDRAZIDES

GEORGETA CARACULACU, I. ZUGRĂVESCU and C. CIOBANU

Institute of Macromolecular Chemistry "Petru Poni", Aleea Gr. Ghica Vodă, Nr. 41 A, Jassy, Rumania

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Abstract—Based on quantitative transformation of unsaturated polyesters into Δ_2 -pyrazoline polymers when reacted with 1.3-dipoles, attempts were made to apply the same reaction to unsaturated polyamides and polyhydrazides having double bonds conjugated with a carbonyl group. One could not obtain heterocyclic polymers because of factors discussed in the paper. The presence of an active hydrogen atom in the molecule of polyamide or polyhydrazide causes a decrease of the dipolarophile capacity of the double bond. Substitution of these hydrogen atoms, both in model compounds and polymers, leads to the expected results. Thus N-alkylpolyamide was quantitatively transformed into the Δ_2 -pyrazoline polyamide.

In a previous paper [1] we described the heterocyclization reaction carried out by a 3+2 dipolar cycloaddition on some reactive polymers such as unsaturated polyesters. New polyesters bearing heterorings, namely Δ_2 -pyrazoline rings, on the backbone were obtained [see Eqn. (1)]:

EXPERIMENTAL

Unsaturated polyhydrazides were prepared by reaction of equimolar amounts of terephthaloyl dihydrazide and fumaroyl chloride in 5% LiCl containing N-methylpyrolidone (NMP). The solution was stirred with cooling. The viscous solution of polymer was allowed to warm to room temperature overnight.

$$\begin{bmatrix}
O & O \\
R - C - CH = CH - C - R'
\end{bmatrix}_{n} + Ph - C = N - N - Ph$$

$$R = R' = OC_{2}H_{4}.$$

$$(1)$$

The present investigation aimed at the application of this 3 + 2 dipolar cyclo-addition to some other unsaturated polymers, such as unsaturated polyamides and polyhydrazides, in order to obtain new polyheterocyclic derivatives, Eqn. (2):

Calcd. for $C_{1.5}H_{1.1}N_4O_4$ — N_{-n}^o 20-4. Found— N_{-n}^o 19-3. Inherent viscosity was 0-18 (measured at 25) for a solution of 0-5 g polymer in NMP with 5% LiCl.

The diphenylnitrilimine (1,3-dipol) was prepared by the method earlier described [2].

$$\begin{bmatrix}
O & O \\
R - C - CH = CH - C - R'
\end{bmatrix}_{n} + Ph - C = N - N - Ph$$

$$R = R' = -NH - NH - ; -NH - .$$
(2)

The capacity of dipole diphenylnitrilimine rapidly to react in situ with unsaturated carboxylic esters forming pyrazoline rings prompted us to use it in a 3+2 cyclo-addition reaction on polyamides and polyhydrazides containing ethylenic bonds conjugated with carbonyl groups.

Diethylfumarate, fumaroyldihydrazide, fumardiamide, fumardianilide. N.N.N'.N'-tetraethylfumaramide and N.N'-diethyl-N.N'-diphenylfumaramide were prepared by literature methods [3–8].

All the Δ_2 -pyrazoline derivatives were prepared thus: to a solution of 1-99 mequiv "double bonds" in 6 ml DMSO

(dimethylsulphoxide) or 1,2-dichloroethane 2 mmole of benzoyl phenyl phenylhydrazide chloride were added. The mixture was heated to 80° . At this temperature, 1 ml triethyl amine was added over 10 min; the mixture was kept at 80° for 2 hr. Finally the reaction mixture was poured into a large excess of water or ethanol; the Δ_2 -pyrazoline derivative was isolated by precipitation and dried in the usual manner.

Calcd. for N.N.N', N'-tetraethyl- Δ_2 -pyrazoline—70·58% C, 13·72% N, 7·84% H; found—69·80% C, 13·40% N, 7·53% H

Calcd. for 3,4-bis(ethylanilide)-2,5-diphenyl- Δ_2 -pyrazoline—76·74% C, 10·84% N, 6·20% H; found—77·16% C, 10·88%N, 6·20% H.

N-Alkyl-polyamide. Piperazine (0.05 mole) and 0.1 mole sodium carbonate were dissolved in 100 ml water at 0°. A solution of 0.05 mole fumaroylchloride in methylene chloride was then quickly added. The solid polymer was filtered off. It is soluble only in phenol.

Calcd. for $C_8H_{10}N_2O_2$ —16.86% N; found—15.25% N. The Δ_2 -pyrazoline derivative was prepared as already described.

RESULTS AND DISCUSSION

In order to obtain information regarding the cyclo-addition on macromolecular compounds, model compounds (I)-(VII) were synthesized to be structurally identical with the repeating units of the unsaturated polymers.

$$H_2N-C-CH=CH-C-NH_2$$
 (III)

$$C_{2}H_{5}$$
 O O $C_{2}H_{5}$
 $N-C-CH=CH-C-N$
 $C_{2}H_{5}$
 $C_{2}H_{5}$

$$C_{6}H_{5}$$
 O O $C_{6}H_{5}$
 $N-C-CH=CH-C-N$
 $C_{2}H_{5}$
 (VI)

$$C_6H_5$$
 O O C_6H_5
 $N-C-CH=CH-C-N$ (VII)
 C_6H_5 C_6H_5 .

It was noticed that the carbonyl groups greatly influence the dipolarophilic character of the ethylenic

group; while the alkoxy substituents enhance the dipolar reactivity of the double bond, hydrazide and amide substituents inhibit the dipolar cyclo-addition.

The tetra-alkyl groups of model compound (V) and the alkyl and phenyl groups of model compound (VI) increase the dipolarophilic reactivity of the double bond compared with compound (VII).

The high dipolarophilic capacity of the double bond of compounds (V) and (VI) was attributed to increased electron density due to the inductive effect and to the hyperconjugation at the carbonyl group strongly polarizing the double bond.

 Δ_2 -pyrazoline adduct could not be obtained when the tetraphenylfumaramide was reacted with the diphenylnitrilimine, probably because of steric hindrance.

As a general conclusion, it may be stated that the exhibited influence of substituents on the dipolarophilic reactivity, decreases in the order:

$$\begin{array}{cccc}
O & O \\
\parallel & \parallel \\
General formula &= R & C & CH & CH & CH \\
\end{array}$$

$$R = \begin{array}{cccc} C_6H_5 & C_6H_5 & C_2H_5 \\ R = & N - & N - & N - & C_2H_5O - \\ C_6H_5 & C_2H_5 & C_2H_5 \\ 0\% & 50\% & 62\% & 100\% \end{array}$$

One can assume also that the cyclo-addition between compounds (II) and (III) and diphenylnitrilimine is influenced by formation of intramolecular hydrogen bonds. This type of hydrogen-bonding does not occur for compounds (V)–(VII).

One can conclude that the polyamides and polyhydrazides, being weak dipolarophilic systems, cannot be transformed into heterocyclic polymers in this way. This transformation might be achieved by replacing the active hydrogen atoms at the nitrogen atom with alkyl groups. This hypothesis was verified by the quantitative heterocyclization of the *N*-alkylpolyamide in a 3 + 2-dipolar cyclo-addition reaction, thus:

$$+ Ph C = N - N - Ph \longrightarrow$$

$$O \qquad O$$

$$C - CH - CH - C - N \longrightarrow$$

$$C \qquad N$$

$$Ph \qquad N \qquad Ph$$

$$(VIII)$$

The structure of N-alkylpolyamide was confirmed by i.r. absorption spectra (Figs. 1 and 2) and elemental analysis.

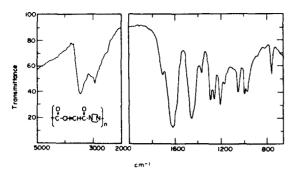


Fig. 1. Infra-red spectra of the N-alkylpolyamide.

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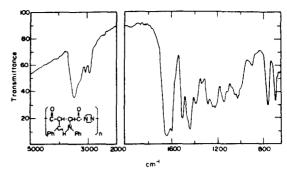


Fig. 2. Infra-red spectra of the $\Delta_2\text{-pyrazoline}$ derivative. Calcd. for $C_{21}H_{20}N_4O_2{=}15{\cdot}55\%$ N; found—16·05% N.

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