

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

POLYAMIDES AND POLYHYDRAZIDES

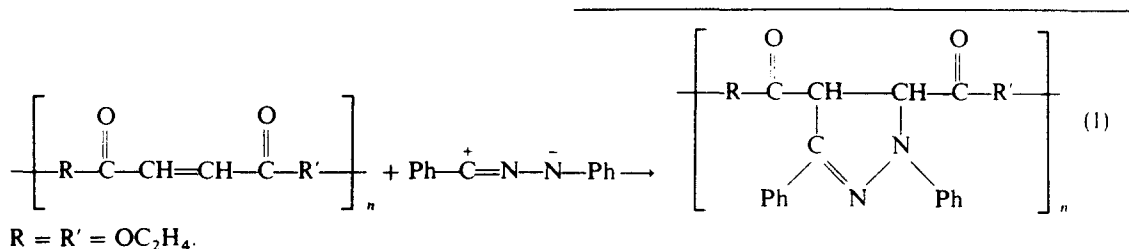
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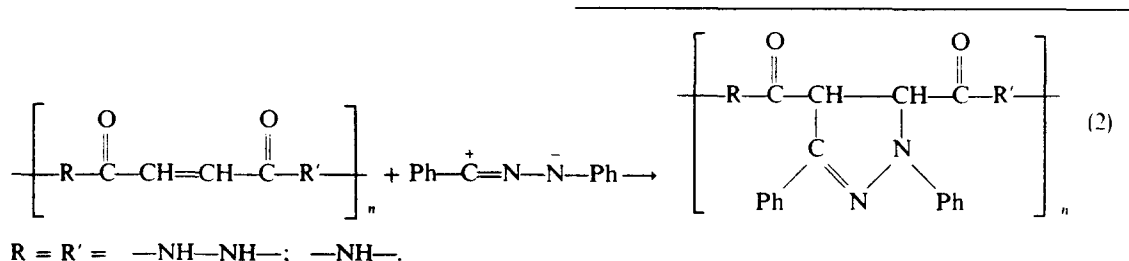
(Received 18 February 1975)

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 cyclo-addition 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)]:



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):



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.

EXPERIMENTAL

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

Calcd. for $\text{C}_{11}\text{H}_{11}\text{N}_4\text{O}_4 \cdot \text{N}^0_n$ 20.4. Found— N^0_n 19.3.

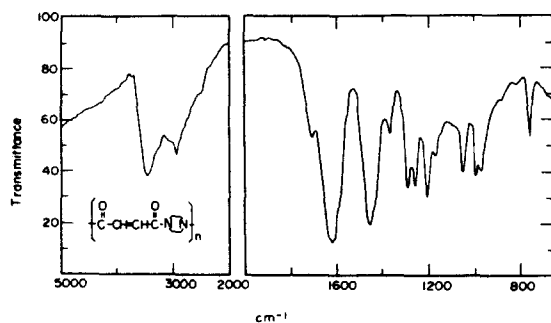
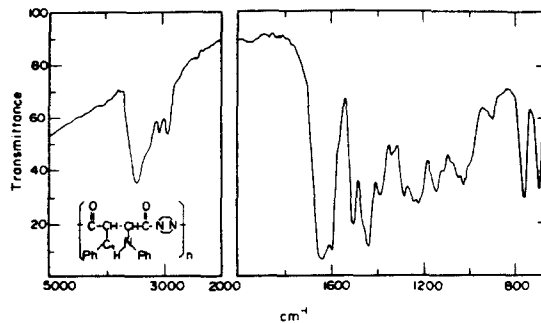
Inherent viscosity was 0.18 (measured at 25°) for a solution of 0.5 g polymer in NMP with 5% LiCl.

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

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

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.Fig. 2. Infra-red spectra of the Δ_2 -pyrazoline derivative. Calcd. for $C_{21}H_{20}N_4O_2$ —15.55% N; found—16.05% N.

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