## SHORT COMMUNICATIONS

# Ring-opening Polymerization of 2-Methyl-1,3,4-oxadiazolin-5-one

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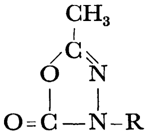
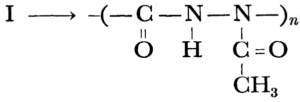
2-Methyl-1,3,4-oxadiazolin-5-ones (I—III) were obtained easily by the reaction of corresponding hydrazides with phosgene in good yield.[1] They were confirmed by elementary analysis and IR spectrum.



I, R=H (mp 112°C)
II, R=$CH_3$ (bp 70—72°C/10mmHg)
III, R=$C_6H_5$ (mp 92—93°C)

It is known that these derivatives are important as antibacterial compounds. The reactions of these compounds with primary amines[2] or water[3] have been reported. We found that a new type polymer IV could be synthesized by the ring-opening polymerization of 2-methyl-1,3,4-oxadiazolin-5-one (I), using tertiary amines or Lewis acids as catalysts. However, 2,4-dimethyl-1,3,4-oxadiazolin-5-one (II) and 2-methyl-4-phenyl-1,3,4-oxadiazolin-5-one (III) did not polymerize.



$$\mathrm{I} \longrightarrow -(-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-\underset{\underset{\underset{CH_3}{|}}{C=O}}{\underset{|}{N}}-)_n-$$

(IV)

Polymerization was carried out in sealed tubes in the absence of oxygen. The conditions for polymerization are given in Table 1. The polymer was purified by means of reprecipitation with *N,N*-dimethylformamide (DMF) and ether. The results are given in Table 1. The yield increases with the increase of the basicity of amines, although the molecular weight of the resulting polymer is low. It was found that a higher concentration of the catalyst is necessary for obtaining high yield. Compound I could also be polymerized by use of Lewis acids such as $BF_3OEt_2$ and $TiCl_4$, but the molecular weight and yield of the polymer obtained were low. The polymer obtained in the form of white powder is soluble in DMF, dimethyl sulfoxide (DMSO) and water, but insoluble in common organic solvents such as alcohol, acetone, and benzene. The structure of the polymer was confirmed by IR and NMR. The IR spectrum (in DMSO) indicated the three characteristic absorption bands at 3100 (N–H), 1720 ($-\underset{\underset{O}{\|}}{C}-CH_3$) and 1690 $cm^{-1}$ ($-\underset{\underset{O}{\|}}{C}-N$). The absorptions attributable to carbonyl group (1770 $cm^{-1}$) and double bond (C=N) (1630 $cm^{-1}$) in the monomer disappeared. NMR spectrum of the polymer shows the two peaks at $\tau=7.35$ (singlet) and $-1.15$ ppm (singlet) assigned to methyl proton and N–H proton, respectively (NMR spectrum of monomer; methyl proton 7.80 ppm, N–H proton $-0.55$ ppm).

Table 1. Polymerization of 2-methyl-1,3,4-oxadiazolin-5-one (I)[a]

| No. | Catalyst[b] | Time (hr) | Temp. (°C) | Conversion (%) | $[\eta]$[c] |
|---|---|---|---|---|---|
| 1 | Triethylenediamine | 30 | 120 | 48.0 | 0.06 |
| 2 | Triethylamine | 30 | 120 | 65.5 | 0.03 |
| 3 | *N,N*-Dimethylbenzylamine | 30 | 120 | 48.0 | 0.07 |
| 4 | Pyridine | 30 | 120 | 25.5 | 0.05 |
| 5 | $AlCl_3$ | 6 | 120 | 1 | 0.03 |
| 6 | $FeCl_3$ | 6 | 120 | 1 | 0.03 |
| 7 | $TiCl_4$ | 6 | 120 | 13 | 0.04 |
| 8 | $BF_3OEt_2$ | 6 | 120 | 10 | 0.07 |
| 9 | *N,N*-Dimethylbenzylamine | 20 | 120 | 93.3 | 0.07[d] |
| 10 | $BF_3OEt_2$ | 10 | 150 | 20 | 0.05 |

a) The polymerization of carried out in bulk.
b) Nos. 1—8, 1 mol% for monomer; Nos. 9—10, 10 mol% for monomer.
c) Measured at 30°C in water.
d) Melting point of this polymer was 224—226°C.

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[1] W. R. Sherman, *J. Org. Chem.*, **26**, 88 (1961).
[2] A. J. Zelauskas and J. A. Aeschlimann, *ibid.*, **20**, 412 (1962).
[3] W. R. Sherman and Anne von Esch, *ibid.*, **27**, 3472 (1962).