
**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

# Oligomeric Carbonothioic Dihydrazides from Dialdehydes and Carbonothioic Dihydrazide

Richard H. Wiley

**To cite this Article** Wiley, Richard H.(1988) 'Oligomeric Carbonothioic Dihydrazides from Dialdehydes and Carbonothioic Dihydrazide', Journal of Macromolecular Science, Part A, 25: 2, 231 — 233
**To link to this Article: DOI:** 10.1080/00222338808051966
**URL:** http://dx.doi.org/10.1080/00222338808051966

J. MACROMOL. SCI.—CHEM., A25(2), pp. 231-233 (1988)

NOTE

# OLIGOMERIC CARBONOTHIOIC DIHYDRAZIDES FROM DIALDEHYDES AND CARBONOTHIOIC DIHYDRAZIDE

RICHARD H. WILEY

8 Roosevelt Circle
Palo Alto, California 94306



There are no previous descriptions of the preparation or properties of oligomeric products from the acid-catalyzed reaction of equimolar proportions of carbonothioic dihydrazide and dialdehydes. Di(alkylidene)carbonothioic dihydrazides are known as the products of the reaction of 1 or 2 mol monofunctional aldehydes [1-3] with 1 mol carbonothioic dihydrazide. The products of the reaction of 1 mol glyoxal bisulfite [4, 5] or kethoxal [5, 6] with 1 or 2 mol carbonothioic dihydrazide have been reported These products are soluble and do not have the properties of the oligomers described here.

This report describes the acid-catalyzed preparation of oligomeric ($n$ = 8 to 10) (diylidene)carbonothioic dihydrazides from equimolar quantities of selected dialdehydes and carbonothioic dihydrazide. The products are formed in acidic aqueous solutions at 70-80°C in essentially quantitative yields and are insoluble in a variety of common solvents. The elemental analyses agree with carboxy/hydrazide termination. This is consistent with termination by traces of carboxaldehyde in the dialdehyde or with terminal oxidation during isolation of the product, or both.

The oligomerization takes place rapidly in acidic media (low pH, excess mineral acid) at 60-85°C. Since mechanistic studies [7] indicate that the reaction of hydrazine derivatives with carbonyl compounds is pH dependent, and optimum at an intermediate value, this oligomerization reaction is unusual among such reactions in operating at a low pH. The oligomers are insoluble in water, dilute acid, pyridine, dimethylformamide, and dimethylsulfoxide. The glyoxal oligomers are soluble in dilute sodium hydroxide

and give intensely colored solutions. The terephthaldehyde oligomer is insoluble in aqueous base and is converted to brilliantly red, insoluble products by aqueous base. The conjugated unsaturation present in the sulfhydryl form functions as the chromophore. The diylidene structure is formulated as =CH–R–CH=; the thiocarbonodihydrazide as =NNHCSNHN=. The oligomer from glyoxal is named oligo[2,2′-ethanediylidene)biscarbonothioic dihydrazide].

## EXPERIMENTAL

Glyoxal (40% aqueous solution) was used as received (Aldrich). Commercial terephthaldehyde (Aldrich) was recrystallized, dried, and stored under nitrogen prior to use. The carbonothioic dihydrazide was used as supplied (Aldrich; EKCo.) or prepared as previously described [2, 8]. Analyses were done by Chemical Analytical Services, University of California, Berkeley.



### Oligo[2,2′-(1,2-ethanediylidene)biscarbonothioic Dihydrazone]

To a solution of 1.06 g carbonothioic dihydrazide in 20 mL water with 1.0 mL concentrated hydrochloric acid (pH 2.6) at 60-70°C is added 1.45 g of 40% glyoxal solution, to which has been added 0.5 mL concentrated hydrochloric acid (pH 1.7). A brown precipitate forms at once. The reaction mixture is heated to 85°C (turns yellow) and cooled (turns green). This solid is collected, washed with water, then with alcohol, and dried to give 1.3 g (theory 1.3 g) of product. This solid is insoluble in water, dimethylsulfoxide, dimethylformamide, pyridine, and dilute acid. It is soluble in dilute aqueous sodium hydroxide to give a dark brown solution. Extracted with warm dimethylsulfoxide, a green material is dissolved, leaving the product (95% recovery) as a black solid. On potentiometric titration the product dissolves (as a weak acid) at pH 8.4, with no significant break in the titration curve, to give a brown solution. Elemental analysis is in agreement with a carboxy/hydrazone-terminated oligomer of 10 units.

Analysis. Calculated for $(C_3H_4N_4S)_{10}H_2O_2$: C, 27.39; H, 3.18; N, 42.58; S, 24.38. Found: C, 27.38; H, 3.50; N, 42.41; S, 24.20.

If conducted in acidified dimethylsulfoxide (the solution is unstable), the reaction is mildly exothermic.

The product is formulated as:

$$HO_2CCH{=}NNHCSNHN{=}(CHCH{=}NNHCSNHN{=})_8CHCH{=}NNHCSNHNH_2$$

**Oligo[2,2'-(1,4-benzenediylidene)biscarbonothioic Dihydrazide]**

To a hot (80°C) solution of 1.0 g carbonothioic dihydrazide in 10 mL water with 1.0 mL concentrated hydrochloric acid is added a solution of 1.34 g terephthaldehyde (recrystallized and stored under nitrogen) in 40 mL water and 10 mL ethanol, also at 80°C. A yellow precipitate forms at once. The mixture is stirred and heated to 85°C. The reaction mixture is cooled to room temperature, and the yellow solid is collected, washed with water and with ethanol, and dried to give 2.0 g product, insoluble in water, ethanol, acetone, dilute sodium hydroxide (in which it turns brilliant red), concentrated hydrochloric acid (yellow), concentrated sulfuric acid, and chromic/sulfuric acid. The analysis conforms to that of an oligomer of eight or nine units with carboxyl termination at both ends of the chain:

$$HO_2CC_6H_4CH{=}NNHCSNHN{=}\left(CHC_6H_4CH{=}NNHCSNHN{=}\right)_8 CHC_6H_4CO_2H$$

Analysis. Calculated for $C_{89}H_{78}O_4N_{36}S_9$: C, 53.33; H, 3.92; N, 25.16, S, 14.39. Found: C, 53.07, H, 4.15; N, 23.54; S, 13.98.



## ACKNOWLEDGMENT

The experimental work was done as a volunteer employee in the Chemistry Department, San Jose State University, San Jose, California.

## REFERENCES

[1] R. Stolle and E. Bowles, *Ber., 41,* 1099 (1908).
[2] N. P. Buu-Hoi, T. B. Loc, and N. D. Xuong, *Bull. Soc. Chim.,* p. 694 (1955).
[3] F. Kurzner and M. Wilkinson, *Chem. Rev., 70,* 116 (1970).
[4] P. Guha and S. De, *J. Indian Chem. Soc., 1,* 141 (1924).
[5] W. C. Kaska, C. Carrano, J. Michelowski, J. Jackson, and W. Levinson, *Bioinorg. Chem., 8,* 225 (1978).
[6] G. Burns, *Inorg. Chem., 7,* 277 (1968).
[7] M. I. Page, in *Organic Reaction Mechanisms* (A. C. Knipe and W. E. Watts, eds.), Wiley, New York, 1981, p. 9; 1982, p. 6.
[8] L. F. Audrieth, E. F. Scott, and P. S. Kipper, *J. Org. Chem., 19,* 733 (1954).

Received June 5, 1987
Revision received July 16, 1987