



TECHNICAL REPORT
NATICK/TR-88/073

AD A 212 076

PROGRESS ON THE PREPARATION AND CHARACTERIZATION OF SOME ALKYNEDIOL OXALATE POLYMERS

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JULY 1988

FINAL REPORT FOR THE PERIOD
MAY 1987 TO AUGUST 1987

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Form Approved
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1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY SEP 07 1989		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NATICK/TR-88/073		7a. NAME OF MONITORING ORGANIZATION	
5a. NAME OF PERFORMING ORGANIZATION U.S. Natick RD&E Center	6b. OFFICE SYMBOL (if applicable) STRNC-YSC	7b. ADDRESS (City, State, and ZIP Code)	
7c. ADDRESS (City, State, and ZIP Code) Kansas St., ATTN: STRNC-YSC Natick, MA 01760-5020		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable)	10. SOURCE OF FUNDING NUMBERS	
7c. ADDRESS (City, State, and ZIP Code)		PROGRAM ELEMENT NO. 62723	PROJECT NO. 1L1AH98
		TASK NO. CA016	WORK UNIT ACCESSION NO. DA311631
1. TITLE (Include Security Classification) Progress on the Preparation and Characterization of Some Alkynediol Oxalate Polymers.			
2. PERSONAL AUTHOR(S) J. W. CULLEN and D. E. REMY			
3a. TYPE OF REPORT Final Report	13b. TIME COVERED FROM 87 May TO 87 Aug	14. DATE OF REPORT (Year, Month, Day) 1988 July 11	15. PAGE COUNT 13
6. SUPPLEMENTARY NOTATION Current affiliation of Mr. Cullen: Monroe Community College, Rochester, NY 14623			
7. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		POLY [(1,4-BUT-2-YNEDIYL) OXALATE], OXALATE POLYMERS, ACETYLENIC POLYMERS, SYNTHESIS.	
9. ABSTRACT (Continue on reverse if necessary and identify by block number)			
Synthetic efforts toward more effective ablative polymers are described. Poly [(1,4-but-2-ynediyl) oxalate] was prepared by transesterification of butyne-1,4-diol and diethyl oxalate. End group analysis by NMR indicated that average molecular weights were low (<1000). Several other synthetic procedures were investigated to increase the molecular weight of the polymer and are discussed. The related diacetylenic polymer poly [1,6-(hexa-2,4-diyne)-diyloxalate], prepared by transesterification, could not be characterized because of the extreme thermal lability of it or a precursor.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David Remy		22b. TELEPHONE (Include Area Code) (508) 651-4722	22c. OFFICE SYMBOL STRNC-YSC

PREFACE

The work described in this report was authorized under work unit 1L162723AH98007 entitled Lazer Hardened Systems for the Individual Protection Program and covers the period from May 1987 to August 1987. The report discusses the progress that was made on the synthesis and characterization of some unsaturated oxalate polymers during this time period.

We wish to express our gratitude to Ms. Gretchen Richard of the Science and Advanced Technology Directorate, U.S. Army Natick Research, Development and Engineering Center and to Ms. Eileen Sullivan of Worcester Polytechnic Institute (WPI) for NMR data and to Dr. Stephen Weininger and Dr. Eleanor Stickles of WPI for valuable discussions.

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TABLE OF CONTENTS

	PAGE
INTRODUCTION	1
RESULTS AND DISCUSSION	3
SUMMARY AND CONCLUSIONS	7
RECOMMENDATIONS	8
REFERENCES	9

PROGRESS ON THE PREPARATION AND CHARACTERIZATION OF SOME ALKYNEDIOL OXALATE POLYMERS

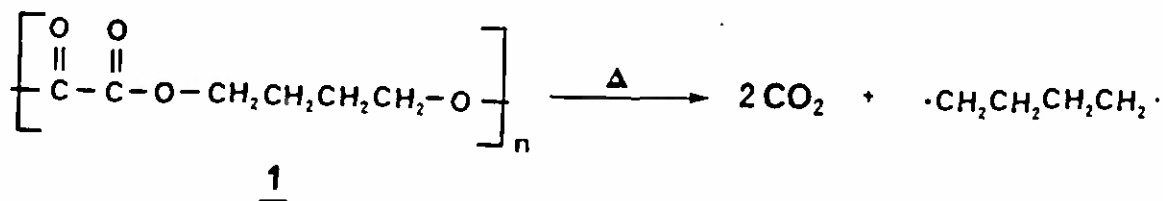
INTRODUCTION

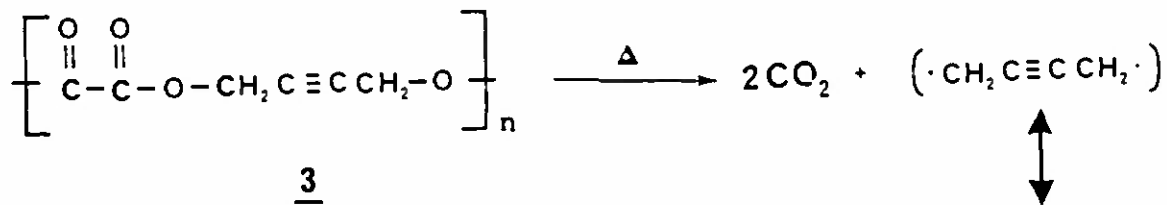
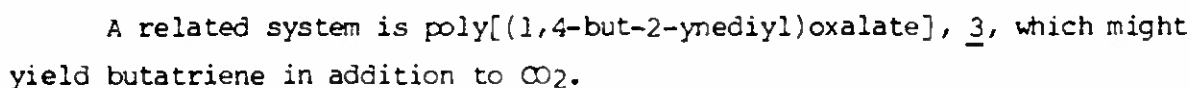
The mechanism and effects of the interaction of high energy laser radiation with polymeric materials are of great interest to the military. One application is in the area of personnel protection from the hazards of directed energy weapons (DEW).

Srinivasan and Leigh¹ have studied the action of far-ultraviolet laser radiation on poly(ethylene terephthalate) (PET) films. Irradiation of the film caused etching of the surface of PET and formed gases such as CO, CO₂, H₂ and volatile organics such as benzene. The absorption of laser radiation leads to a very high concentration of free radicals in the surface layers of the PET film shortly afterward. The photoproducts (possibly in vibrationally excited states) are then ejected from the film surface and probably carry away the excess energy of the photon pulse. The result is that the photoetched film undergoes no significant temperature increase. Srinivasan and Leigh term this process an "ablation".

Polyesters or polycarbonates should afford a greater degree of protection from a CO₂ laser than other polymer types. Oxalate esters should be even more attractive candidates as ablative polymers because they absorb light at lower energies than ordinary esters² (λ_{max} diethyl oxalate, 244 nm). In addition, on degradation these polymers will release two CO₂ units per repeat unit rather than one, which may increase the ablation energy per unit area of the polymer surface.

Thermal degradation of an oxalate polymer such as poly[(1,4-butane-diyl)oxalate] 1 should yield carbon dioxide and the 1,4-butanediyl diradical.

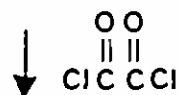
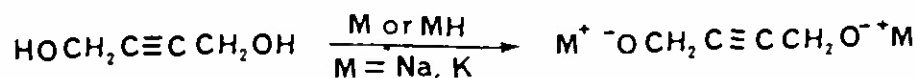
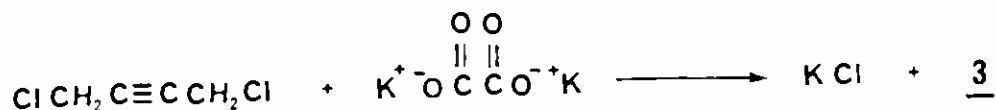
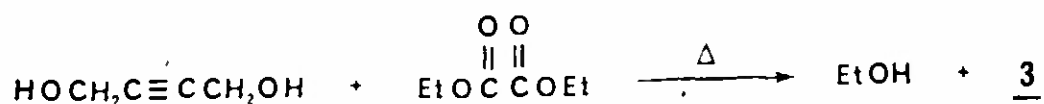


$$\left[\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C} - \text{C} - \text{O} - \text{CH}_2\text{CH}=\text{CHCH}_2 - \text{O} \end{array} \right]_n \xrightarrow{\Delta} 2\text{CO}_2 + (\cdot\text{CH}_2\text{CH}=\text{CHCH}_2\cdot)$$


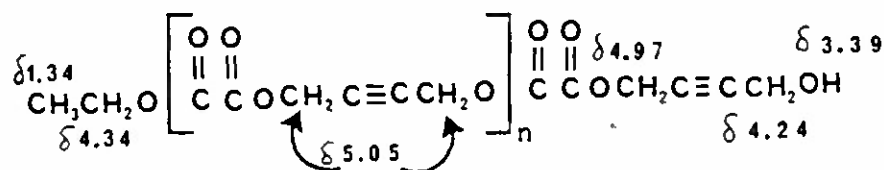
RESULTS AND DISCUSSION

This report will focus on synthetic approaches to oxalate polymers containing triple bonds such as 3. While a very large number of linear polyesters have been prepared since the work of Carothers,³ only a few linear polyesters containing triple bonds have been synthesized. One of the reasons for this is that synthesis of such linear polyesters is complicated by side reactions leading to crosslinking.⁴

Three possible methods for the preparation of oxalate polymers were considered. These three approaches are shown below, using polyoxalate 3 to illustrate.



A transesterification procedure has been developed by E. Stickles, S. Weininger, and D. Remy⁵ and used to prepare a number of different polyoxalates. A slight modification of this procedure was used to prepare 3. Equimolar amounts of 2-butyne-1,4-diol* and diethyl oxalate and approx. 1% of stannous octanoate catalyst (no reaction occurred in the absence of catalyst in this case) were heated at 90-100°C for 6 hr. with a stream of N₂ bubbling through. The reaction mixture was then placed in a vacuum oven at 90°C/0.1mm for 16 hr. The polymer was precipitated by dissolving the viscous brown liquid in acetone and adding the acetone solution to an excess of hexane. The cream-colored polymer 3 was washed several times with hexane. The yield of 3 was 75%. On heating, the product melted between 70 and 90°C and effervesced above 140°C, possibly indicating further polymerization. The infrared spectrum of 3 showed a strong carbonyl stretch at 1750 cm⁻¹. The proton NMR spectrum (acetone-d₆) of 3 shows that the polymer molecules are capped with both alcohol and ethyl ester groups. NMR assignments are as follows:



End group analysis by NMR integration indicates that there are an average of six repeat units per molecule and that the average molecular weight is less than 1000.

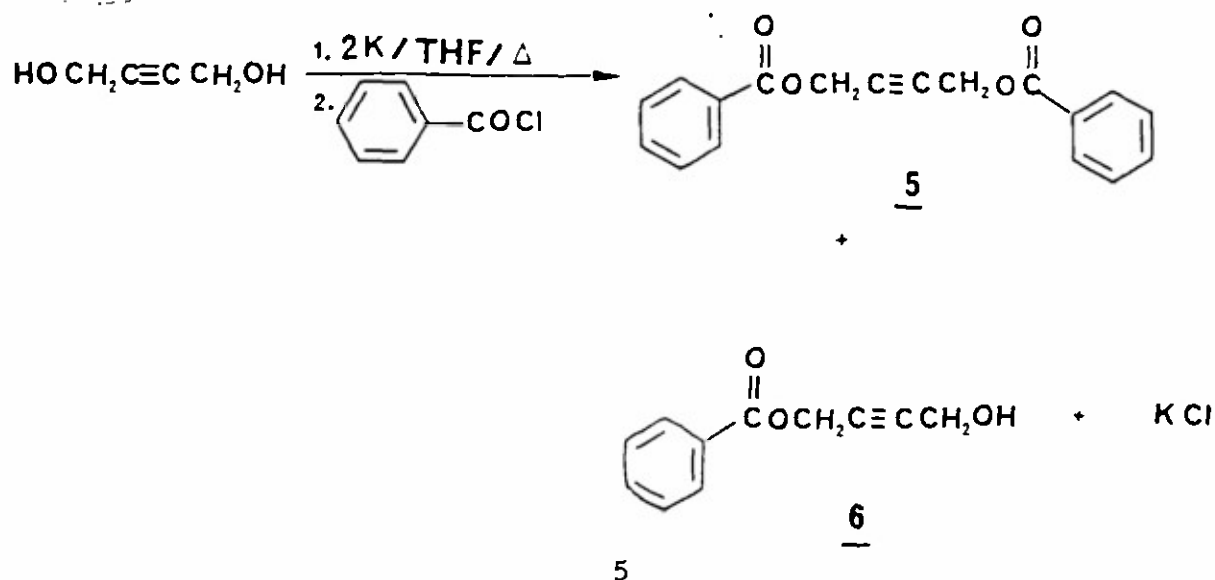
The low degree of polymerization seen here was also observed by Stickles et al. in the NMR end group analysis of oxalate polymers 1 and 2 prepared by transesterification. Feit, Raucher and Zilkha⁴ also report low molecular weights in the preparation of acetylenic polyesters.

Two other problems have been encountered with the transesterification method of synthesis. An attempt was made to prepare poly[1,6-(hexa-2,4-diyne)-diyloxalate] 4 by transesterification of diethyl oxalate and hexa-2,4-diyne-1,6-diol. When the reaction mixture was heated in the vacuum oven at 80°C, the sample detonated. Apparently the diacetylenic polymer 4 is much more thermally labile than 3 and does not survive the temperatures required for the

*Commercial 2-butyne-1,4-diol is impure and may be purified by the procedure described in reference 4 or by several recrystallizations from ethyl acetate.

Because of these difficulties with the transesterification method it was decided to investigate the other two possible synthetic methods. The reaction of potassium oxalate with 1,4-dichloro-2-butyne should give 3 and KCl. However, the difficulty here is dissolving both reagents in a solvent medium. An attempt was made to carry out a reaction between 1,4-dichloro-trans-2-butene and anhydrous potassium oxalate in the presence of a crown ether. However, potassium oxalate did not dissolve in dioxane even after two equivalents of 18-crown-6 had been added. Nonetheless, the dichloride was added, but no reaction occurred.

Conversion of 2-butyne-1,4-diol to the corresponding dialkoxide proved to be more difficult than anticipated. Reaction with sodium or sodium hydride at room temperature in glyme or tetrahydrofuran (THF) did not give significant quantities of dialkoxide. It was decided to check for the formation of dialkoxide by quenching with benzoyl chloride.



2-Butyne-1,4-diol was treated with two equivalents of potassium in refluxing THF followed by addition of two equivalents of benzoyl chloride. After filtration to separate the KCl, the solvent was removed by spin evaporation in vacuo. The resulting yellow oil was dissolved in ether and washed twice with saturated NaHCO₃. After drying over MgSO₄, the ether was evaporated to give an oil which proved to be a mixture of dibenzoate 5 and monobenzoate 6. The two compounds were easily separated by column chromatography on silica gel by eluting with chloroform. The structures of 5 and 6 were confirmed by their NMR spectra (CDCl₃).

Dibenzoate 5:

<u>ppm</u>	<u>Multiplicity</u>	<u>Integration</u>	<u>Assignment</u>
8.10	d	4H	ortho-H
7.48	d of d	6H	meta and para-H
4.99	s	4H	CH ₂

Monobenzoate 6:

<u>ppm</u>	<u>Multiplicity</u>	<u>Integration</u>	<u>Assignment</u>
8.06	d	2H	ortho-H
7.42	d of d	3H	meta and para-H
4.93	s	2H	CH ₂ (nearest ester)
4.33	s	2H	CH ₂ (nearest alcohol)
3.77	s	1H	OH

The yields of dibenzoate 5 and monobenzoate 6 were 78% and 9.5%, respectively.

When 2-butyne-1,4-diol was treated with two equivalents of potassium as before, followed by addition of one equivalent of oxalyl chloride, a viscous brown liquid was obtained that was identified as the desired oxalate polymer 3 on the basis of the similarity of its IR spectrum (C=O at 1750 cm⁻¹, liq.

film) and NMR spectrum (acetone- d_6) to the product from the esterification procedure. However, end group analysis indicated that the product was of lower average molecular weight than that obtained by the transesterification method. In addition, attempts to precipitate out the product were unsuccessful.

An attempt was made to prepare the diacetylenic polymer 4 via the dialkoxide method. Hexa-2,4-diyne-1,6-diol was treated with potassium in refluxing THF followed by addition of oxalyl chloride. The major product from this reaction was a dark brown solid which was insoluble in water and a variety of organic solvents. It was concluded that extensive crosslinking and/or reduction of the triple bonds had occurred. It was thought that by using sodium hydride rather than potassium to form the dialkoxide that reduction of the triple bonds would be much less likely. The feasibility of using sodium hydride to generate the dialkoxide was shown by an experiment in which treatment of 2-butyne-1,4-diol with NaH in refluxing THF followed by addition of benzoyl chloride gave the dibenzoate 5 and the monobenzoate 6 in approximately the same ratio as the procedure using potassium.

SUMMARY AND CONCLUSIONS:

It has proved possible to prepare poly[(1,4-but-2-ynediyl)oxalate] (3) by transesterification of but-2-yne-1,4-diol and diethyl oxalate. However, the polymer is of low molecular weight and it has been found that more hindered secondary and tertiary diols do not react. In addition, the temperatures required for the reaction are too high for the formation of the diacetylenic polymer 4, which is apparently thermally labile.

For these reasons an alternative synthesis involving reaction of a dialkoxide with oxalyl chloride was investigated. The method was shown to be viable by reactions in which but-2-yne-1,4-diol reacted with sodium hydride or potassium in THF and was quenched with benzoyl chloride. However, in these reactions a substantial amount of monosubstituted product was seen, indicating that a considerable amount of monoalkoxide was present in addition to the dialkoxide. This may account for the low molecular weight found in the reaction with oxalyl chloride. In addition, the low degree of polymerization may be due to the very low solubility of the alkoxide in THF.

RECOMMENDATIONS

It is suggested that the alkoxide method of oxalate polymer preparation be explored in more depth in order to improve yields and increase average polymer molecular weight. Some possible changes in the procedures might be: using an excess of sodium hydride or longer reaction time to ensure complete conversion to the dialkoxide, and trying other solvents (e.g. glyme, DMF, DMSO) in which the dialkoxide might be more soluble than in THF. Also, the reaction with 2,4-hexadiyne-1,6-diol and with more hindered alcohols such as 3-hexyn-2,5-diol and 2,5-dimethyl-3-hexyn-2,5-diol should be attempted. If these reactions can be made to proceed smoothly, the dialkoxide method of synthesis will prove to be a useful method for the synthesis of oxalate polymers.

This document reports research undertaken at the US Army Natick Research, Development and Engineering Center and has been assigned No. NATICK/TR-88/073 in the series of reports approved for publication.

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