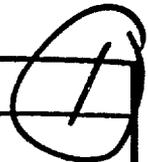


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1a. REPORT SECURITY CLASSIFICATION none		2a. SECURITY CLASSIFICATION AUTHORITY none		3. DISTRIBUTION/AVAILABILITY OF ABSTRACT none		4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 35		5. MONITORING ORGANIZATION REPORT NUMBER(S) ONR N00014-89-J-1225	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE none		6a. NAME OF PERFORMING ORGANIZATION University of Southern Mississippi		6b. OFFICE SYMBOL (if applicable)		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 North Quincy Street Arlington, VA 22217-5000	
6c. ADDRESS (City, State, and ZIP Code) University of Southern Mississippi Department of Polymer Science Hattiesburg, MS 39406-0076		8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		10. SOURCE OF FUNDING NUMBERS	
8c. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 North Quincy Street Arlington, VA 22217-5000		PROGRAM ELEMENT NO.		PROJECT NO.		TASK NO.		WORK UNIT ACCESSION NO.	
11. TITLE (Include Security Classification) Radical Homopolymerization of a Trisubstituted Alkene: 1-Cyclobutenecarboxylic Acid and its Polymer.									
12. PERSONAL AUTHOR(S) Paul K. Casey and Lon J. Mathias									
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 6-1-89 TO 5-31-90		14. DATE OF REPORT (Year, Month, Day) 1990, June 18		15. PAGE COUNT			
16. SUPPLEMENTARY NOTATION Submitted for publication in <u>Polymer Communications</u>									
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)						
FIELD	GROUP	SUB-GROUP	Homopolymerization, Trisubstituted Alkene, 1-Cyclobutenecarboxylic Acid, Polymers, Composite materials (JG)						
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Unexpected formation of an insoluble polymer during purification of 1-cyclobutenecarboxylic acid led to solid state ¹³ C NMR characterization which seemed to indicate vinyl polymerization was occurring. Deliberate attempts to induce radical polymerization involved photoinitiation with 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651) in N,N-dimethylformamide (DMF) or tetrahydrofuran (THF) to give a product that was soluble in dimethylsulfoxide (DMSO) and very soluble in aqueous base. Spectral characterization with ¹³ C NMR in solution (DMSO-d ₆) and CP/MAS confirmed vinyl polymerization and the presence of pendent carboxylic acid groups. Notably absent were peaks due to ester linkages and backbone or pendent unsaturation. Intrinsic viscosities of the potassium salt of the polymer in pure water and in 1 N aqueous NaCl were ca 2.25 g/dL and 0.27 g/dL, respectively, consistent with a polyelectrolyte effect in water and a reasonable molecular weight. grams per deciliters									
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input checked="" type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS					21. ABSTRACT SECURITY CLASSIFICATION				
22a. NAME OF RESPONSIBLE INDIVIDUAL Lon J. Mathias					22b. TELEPHONE (Include Area Code) 601-266-4871		22c. OFFICE SYMBOL		

OFFICE OF NAVAL RESEARCH

Contract N00014-89-J-1225

Technical Report No. 35

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by

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Submitted for publication in

Polymer Communications

Department of Polymer Science
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Southern Station Box 10076
Hattiesburg, MS 39406-0076

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Abstract

Unexpected formation of an insoluble polymer during purification of 1-cyclobutenecarboxylic acid led to solid state ^{13}C NMR characterization which seemed to indicate vinyl polymerization was occurring. Deliberate attempts to induce radical polymerization involved photoinitiation with 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651) in N,N-dimethylformamide (DMF) or tetrahydrofuran (THF) to give a product that was soluble in dimethylsulfoxide (DMSO) and very soluble in aqueous base. Spectral characterization with ^{13}C NMR in solution (DMSO- d_6) and CP/MAS confirmed vinyl polymerization and the presence of pendent carboxylic acid groups. Notably absent were peaks due to ester linkages and backbone or pendent unsaturation. Intrinsic viscosities of the potassium salt of the polymer in pure water and in 1 N aqueous NaCl were ca 2.25 g/dL and 0.27 g/dL, respectively, consistent with a polyelectrolyte effect in water and a reasonable molecular weight.



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Introduction

Cyclobutene-containing monomers, oligomers, and polymers have proven to be excellent candidates for high performance matrix systems for composite materials. Benzocyclobutene derivatives can give mostly or wholly hydrocarbon matrices^{1,2}, while use of 1,2-disubstituted cyclobutenes incorporated into polyamides^{3,4} two give heterofunctional resins. Both systems alleviate the need for strict component mixing while providing increased resin pot life and high crosslink density. Since cyclobutenes ring open to form a diene at elevated temperatures, materials containing the cyclobutene moiety can be thermally cured in several ways⁵ (Figure 1). The dienes can undergo radical polymerization or Diels-Alder reactions with itself or other dieneophiles deliberately incorporated into the resin system. Cyclobutene-terminated monomers and reactive oligomers should also form composite matrices that would benefit from these many cure pathways.

During the synthetic work-up of 1-cyclobutenecarboxylic acid we were surprised to see spontaneous formation of a polymer at ambient temperature. Search of the literature revealed previous work of Hall⁶ and Gale⁷ on the addition polymerization of several cyclobutene derivatives. Their work with 1-bicyclobutanecarbonitrile and 1-cyclobutenecarbonitrile involved attempts to produce polymers similar to polyacrylonitrile from less toxic monomers. Apparently, no deliberate attempts to polymerize 1-cyclobutenecarboxylic acid have been reported, although homopolymerizations of 1-cyclobutenecarbonitrile and methyl cyclobutene-1-carboxylate using a variety of free radical methods were briefly mentioned.⁴ In addition, Cambell and Rydon described the

synthesis of 1-cyclobutenecarboxylic acid yielding a product that polymerized due to adsorption of atmospheric oxygen; no analytical data on this polymer was given.⁸ Other research with cyclobutene derivatives has involved their use as intermediates in the synthesis of several natural products.^{9,10,11,12,13} We describe here our efforts to polymerize 1-cyclobutenecarboxylic acid under controlled conditions and characterize the homopolymer obtained.

Experimental

1-Cyclobutanecarboxylic acid was synthesized using a modified procedure of Cason and Allen¹⁴. Substitution of ethanol by methanol and 1,3-dibromopropane by 1-bromo-3-chloropropane produced dimethyl 1,1-cyclobutanedicarboxylate instead of the diethyl ester. Acid hydrolysis to 1,1-cyclobutanedicarboxylic acid and subsequent thermal decarboxylation to 1-cyclobutanecarboxylic acid was performed as described¹² with a reproducible overall yield of 25 percent.

Methyl 1-bromo-1-cyclobutanecarboxylate was synthesized using a reported procedure⁶ for free radical bromination of 3,3-dimethyl-1-cyclobutanecarboxylic acid. A reproducible yield of 85 percent was obtained when 1-cyclobutanecarboxylic acid was substituted.

1-Cyclobutenecarboxylic acid was synthesized as earlier described⁶ using refluxing toluene and molten KOH to eliminate HBr from 1-bromo-1-cyclobutanecarboxylic acid with a reproducible yield of 62 percent.

Photopolymerization was performed by exposing a DMF or THF solution of 1-cyclobutenecarboxylic acid (25 wt%) and 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651 at 1 wt% of the monomer) to a 365 nm UV fluorescent lamp for 15 min. The polymer was recovered from the resulting gelatinous solution by precipitation, filtration, soxhlet extraction with THF for 24 hours, and drying under high vacuum at ambient temperature.

Characterization of the synthetic intermediates, monomers, and polymers was performed using solution NMR (Bruker Instruments AC-300); solid state NMR (Bruker Instruments MSL-200); thermal analysis (Dupont 9900 thermal analyzer equipped with a 910 DSC module); and dilute solution viscosity (#100 Cannon-Ubbelohde constant dilution semimicro viscometer).

Results and discussion

Polymerization of 1-cyclobutenecarboxylic acid could proceed by three different mechanisms (Figure 2). Free radical addition through the strained double bond would give a polymer containing cyclobutane repeat units with pendent carboxylic acids. Polymerization through Michael polyaddition would give a cyclobutane-containing polyester. Ring-opening of the cyclobutene monomer would give a 2-substituted diene that could polymerize radically to form 1,4- or 1,2-addition polymer with carboxylic acid pendent groups.

There is no spectroscopic evidence to support either the Michael route or free radical polymerization of the ring-opened cyclobutene. The absence of a ^{13}C resonance for an ester C-O carbon around 60 ppm for the polymer in both the solution and solid

state NMR spectra eliminates the Michael polycondensation process. Similarly, no alkene carbon peaks, required for the butadiene polymer were observed. In addition, differential scanning calorimetry of the monomer reveals a melting endotherm at 62.5 °C and an exotherm for ring-opening at 170-180 °C. Since both the spontaneous and photoinitiated polymerizations take place readily at ambient temperature, ring-opening before polymerization is not likely. Furthermore, polymerization through the diene would likely yield crosslinked polymer due to backbone and pendent alkene groups. Since the polymer was soluble in DMSO and in one equivalent of aqueous KOH, it is not crosslinked and must contain pendent carboxylic acid groups.

Comparison of the solution and solid state ^{13}C NMR spectra of the monomer and polymer (Figures 3 and 4) support polymerization of 1-cyclobutenecarboxylic acid to a trisubstituted ethane polymer (residual THF was difficult to remove with anhydride formation and crosslinking). The disappearance of the alkene carbon peaks of the monomer coupled with the absence of alkene carbon peaks in the product is consistent only with a cyclobutane repeat unit. In both the solution and solid state NMR's, the downfield shift and broadening of the carbonyl peaks is also consistent with polymerization of a strained alkene carboxylic acid with loss of conjugation. A reproducible Tg of 83 °C is obtained when the polymer is heated to 150 °C at 10 degrees/minute, while polymer decomposition occurs above 225 °C. An estimated intrinsic viscosity of 2.25 g/dl for the polymer was obtained for an aqueous solution containing 1 equivalent of KOH; a pronounced polyelectrolyte effect was observed (Figure 5). Repeating the viscosity experiment using 1N aqueous NaCl as the solvent results in straight-line plots with an intrinsic viscosity of 0.27 g/dl.

Few 1,2-di-, tri- and tetra-substituted alkenes undergo radical homopolymerization due to steric repulsions of the approaching monomer by substituents on the ultimate carbon. However, the presence of substituents on every carbon of oligomers from such monomers inhibits both monomer addition and radical termination. The latter may be the reason that 1-substituted cyclobutenes can form polymer; i.e. polymer formation is the more favorable of the two unfavorable reaction paths. An additional driving force for the addition polymerization of cyclobutene is the relief of ring strain by polymerization through the distorted double bond. In any event, the ready photopolymerization of this monomer extends the family of cyclobutene derivatives that undergo vinyl polyaddition to give novel polymers containing backbone cyclobutane units and, in this case, a reactive carboxylic acid functional group.

Acknowledgements

We gratefully acknowledge a Department of Defence instrumentation grant with which we purchased our Bruker MSL-200 spectrometer and a grant from the United States Department of Agriculture with which we purchased our Bruker AC-300 spectrometer. This research was supported in part by a grant from the Office of Naval Research.

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Figures

- Figure 1** Possible thermal cure pathways for cyclobutene derivatives.
- Figure 2** Three possible polymerization pathways available to 1-cyclobutenecarboxylic acid.
- Figure 3** DMSO- d_6 solution ^{13}C NMR of 1-cyclobutenecarboxylic acid monomer (bottom trace) and soxhlet purified (THF) polymer (top trace).
- Figure 4** Solid state ^{13}C NMR spectrum of 1-cyclobutenecarboxylic acid monomer (bottom trace) and soxhlet purified (THF) polymer (top trace).
- Figure 5** Viscosity plots of the potassium salt of poly(1-cyclobutenecarboxylic acid) in water (upper two traces) and in 1N NaCl (lower two traces).

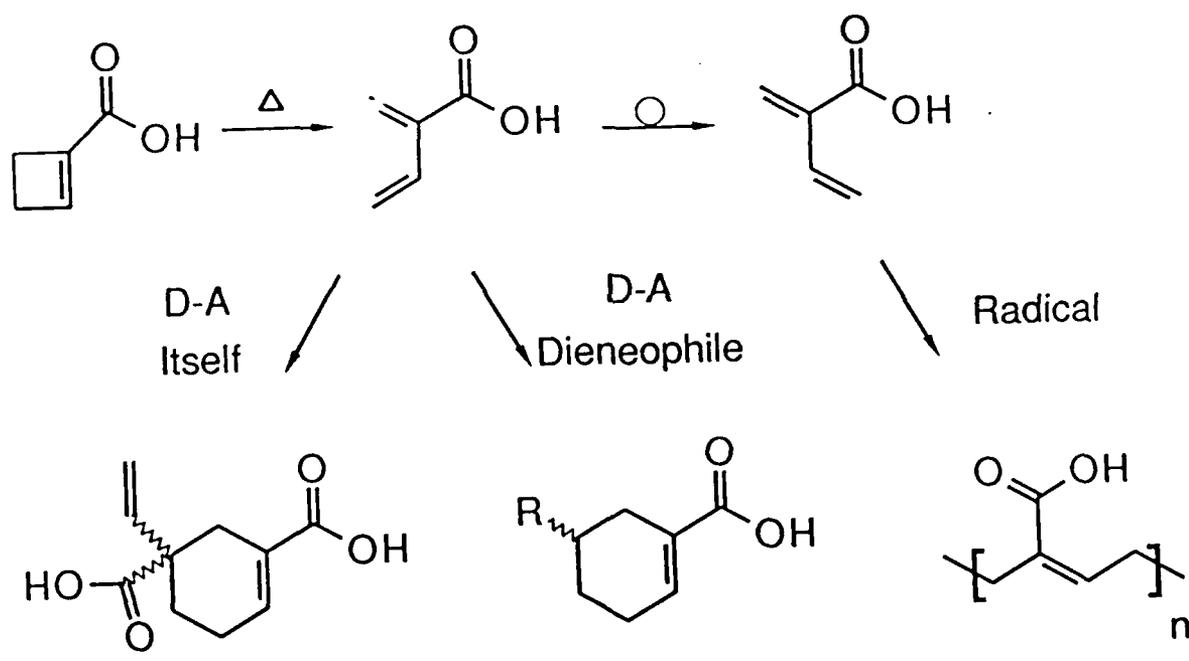


Fig 1

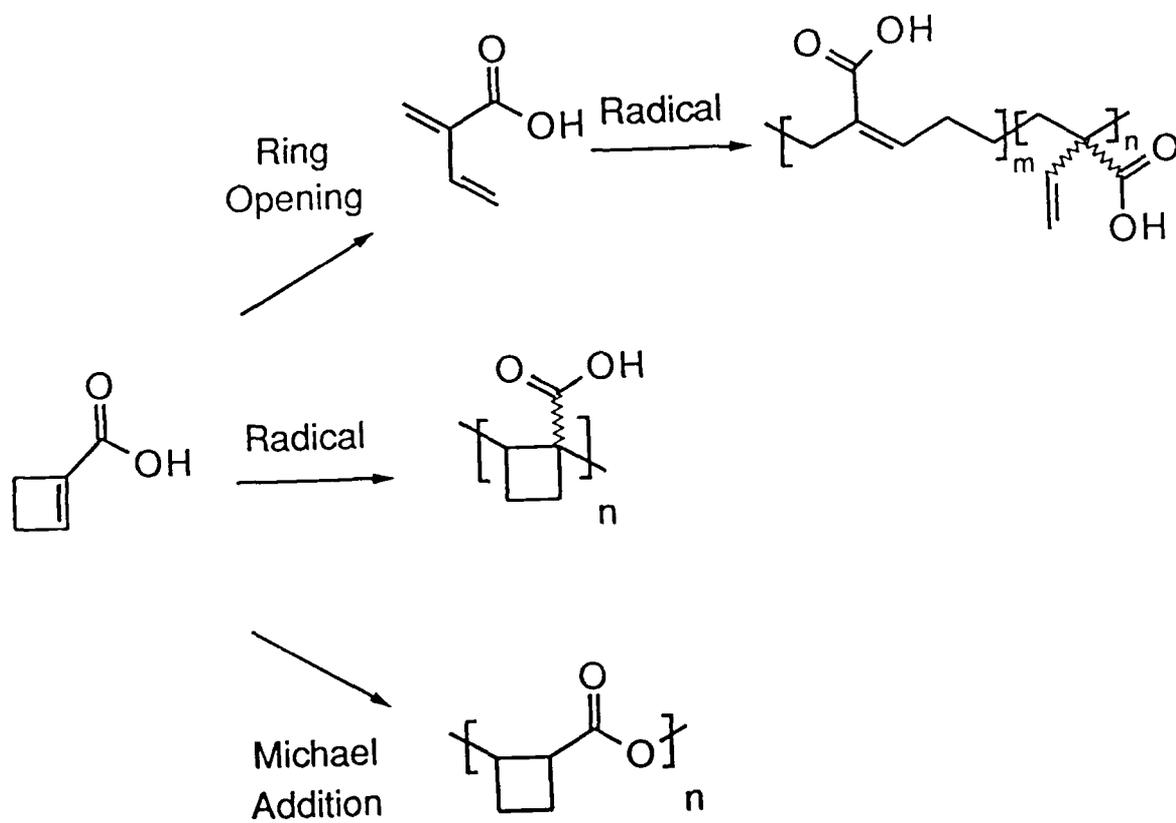
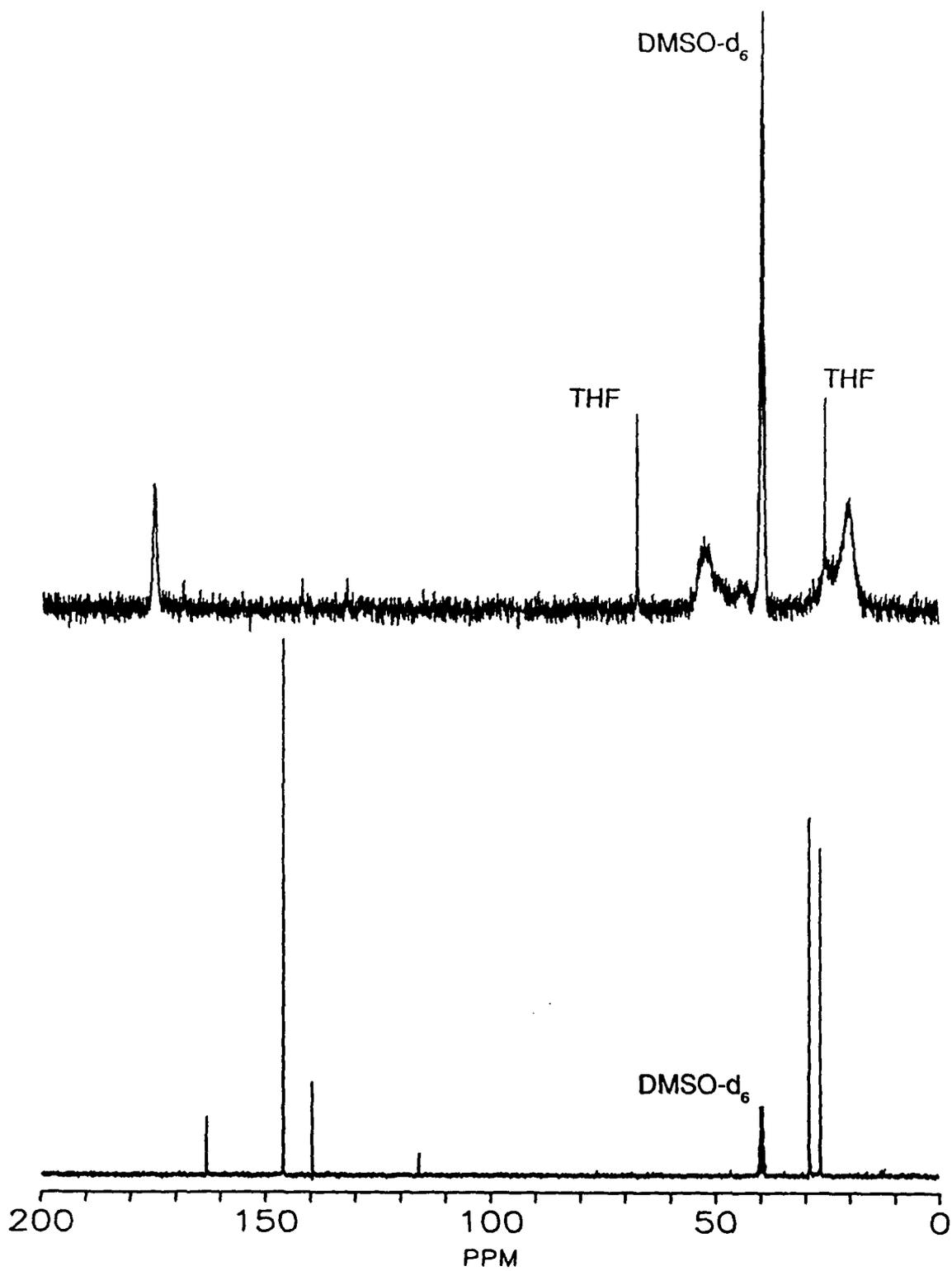
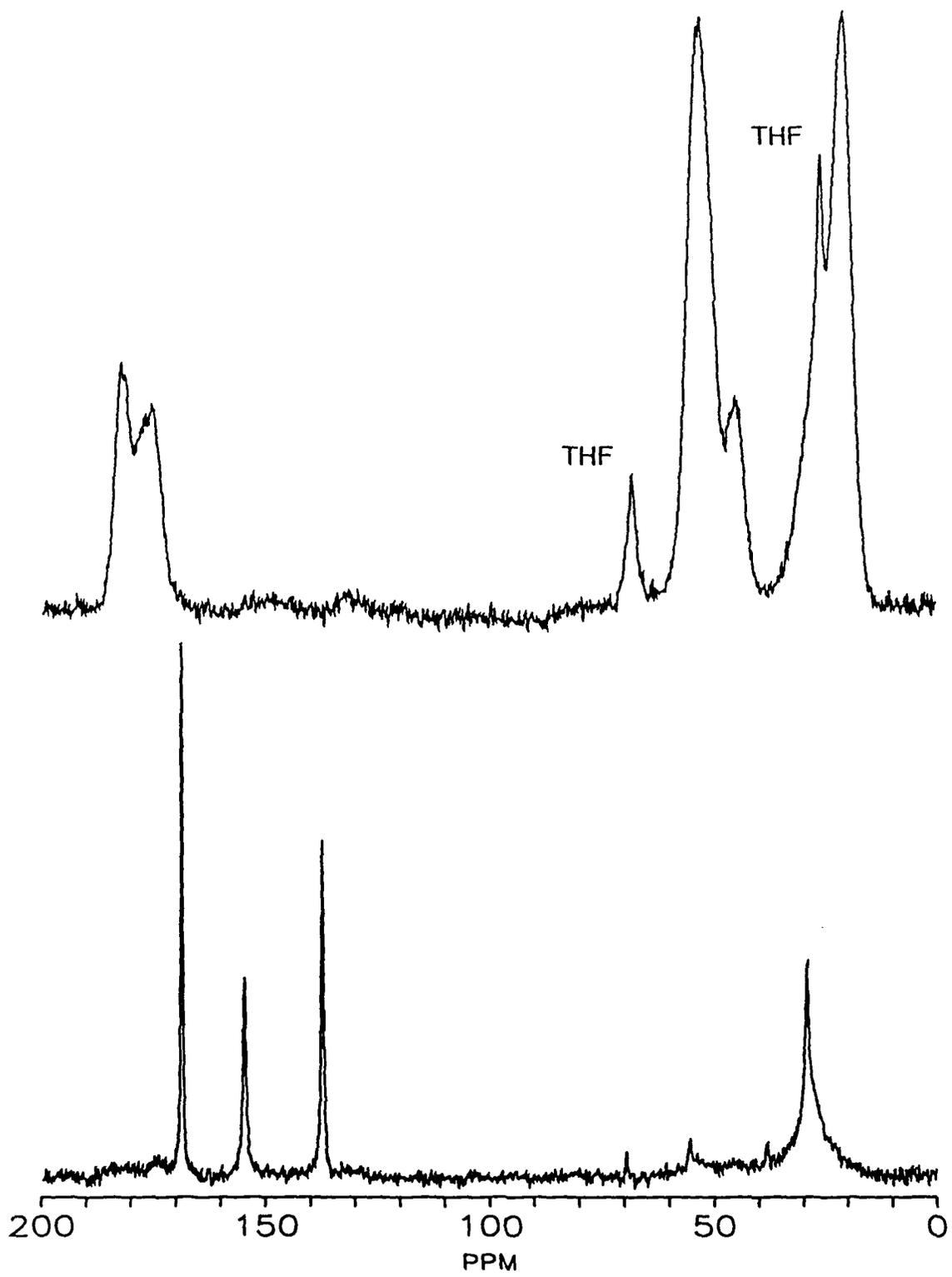


Fig 2



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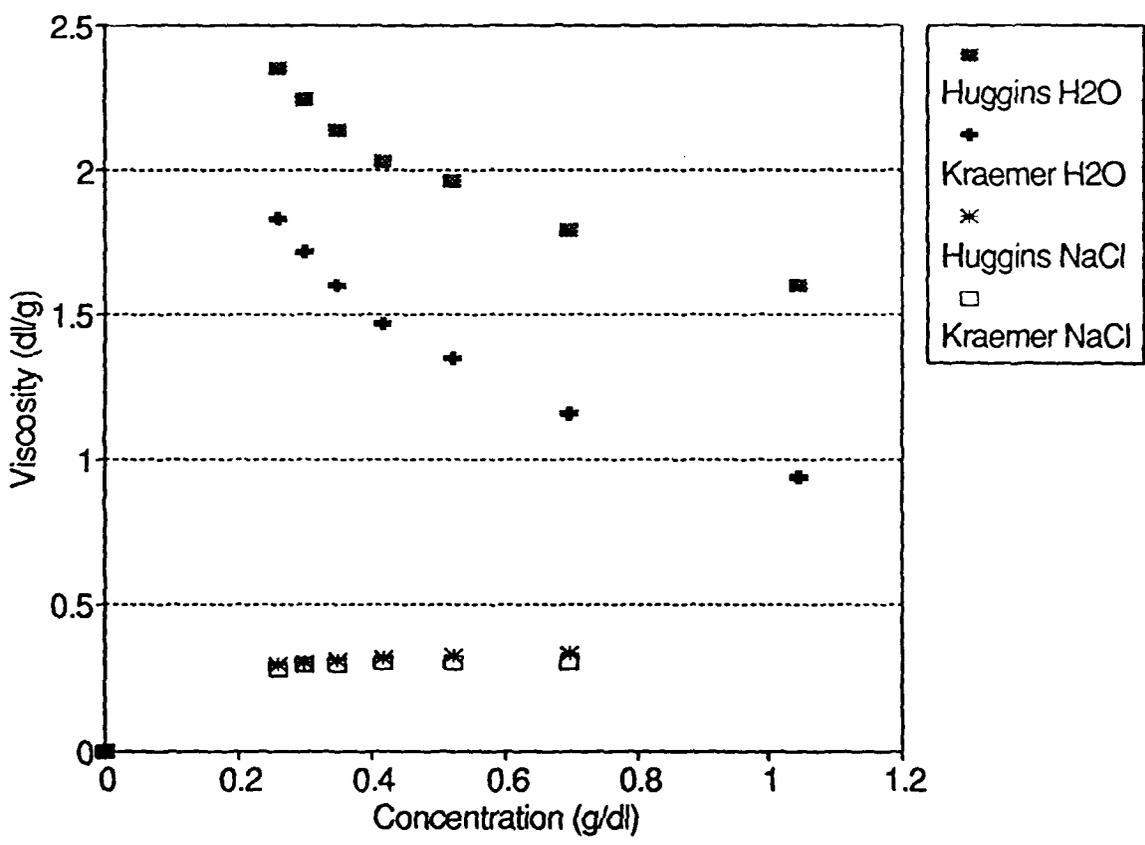


Fig 5