

TRANSFORMATION OF SUCROSE
(PREPARATION AND CHARACTERIZATION OF
SUCROSE POLYESTERS OF DICARBOXYLIC ACID)

by
SUNIL KUMAR MATTEY
DEPARTMENT OF CHEMISTRY

Submitted
in fulfillment of the requirements of the degree of
DOCTOR OF PHILOSOPHY



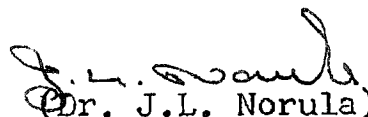
to the
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
September 1984

*Dedicated to my
Parents*

C E R T I F I C A T E

This is to certify that the thesis entitled, "Transformation of Sucrose (Preparation and Characterisation of Sucrose Polyesters of Dicarboxylic Acids)", being submitted by Mr. Sunil Kumar Matthey to the Indian Institute of Technology, Delhi for the award of the Degree of 'Doctor of Philosophy in Chemistry', is a record of bonafide research work carried out by him. Mr. Sunil Kumar Matthey has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.


(Dr. J.L. Norula)
Research Supervisor

A C K N O W L E D G E M E N T

I hereby extend my heartfelt gratitude to my research supervisor Dr. J.L. Norula for being the major source of inspiration, a constant support and a valuable guiding force.

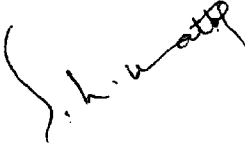
My thanks are due to Prof. N.K. Jha and Prof. R.P. Gandhi for providing all the necessary facilities throughout the course of the work.

I am highly indebted to Ms. Padmaja Nair for the support, companionship and help rendered by her.

I shall use this opportunity to express my special thanks to Dr. M.S.M. Rawat, Mr. M.P. Singh Ishar, Mr.A.C. Misra and all my friends and colleagues for the friendly co-operation extended by them.

A special note of gratitude to all the laboratory staff for their help at various stages of work.

Mr. Jagdish Kumar will be friendly remembered for his accurate and neat typing.


(SUNIL KUMAR MATHEY)

A B S T R A C T

This thesis deals with the Synthesis and Characterization of Poly(sucrose esters). Sucrose (1 mole) was condensed with adipic sebacic and terephthalic acid chlorides/esters (in 2, 4, 6 and 8 moles respectively) by solution, interfacial and transesterification polycondensation methods.

The samples prepared were characterized by end group analysis, density measurements, solubility and chemical resistance studies, viscosity measurements, infrared spectroscopy (both qualitative and quantitative), quantitative nuclear magnetic resonance and elemental analysis. Thermal behaviour was investigated by thermogravimetric analysis in nitrogen and air atmosphere and differential thermal analysis in air.

It was observed that properties of poly(sucrose esters) were much dependant on the method of their synthesis. Transesterification polycondensation was found to be best approach, since it resulted in isolable soluble products. The slow reaction rate of transesterification also helped in monitoring the reaction and isolation of products at various stages. The interfacial

and solution polycondensation were seen to undergo side reactions besides forming insoluble and infusible products.

End group analysis showed decrease in hydroxyl number with increase in composition ratios of the reactants. An increasing composition ratio was also seen to result in an increase of acid number in case of interfacial and solution polycondensation products.

Intrinsic viscosity $[\eta]$ of the samples were found to be decreasing with increasing composition ratios. Among three poly(sucrose esters), poly(sucrose adipates) showed maximum $[\eta]$. Density measurements showed higher values for poly(sucrose terephthalates) as compared to other samples. Density of the poly(sucrose terephthalates) prepared by solution and interfacial polycondensation were found to be increasing with increasing composition ratios, whereas all other samples showed a decreasing pattern. Quantitative IR and NMR studies of poly(sucrose terephthalates) prepared by transesterification polycondensation revealed the mole fraction of acid incorporated into the samples.

Thermal studies (TGA) indicated higher stability for poly(sucrose terephthalates) than poly(sucrose

adipates) and poly(sucrose sebacates). DTA studies showed only exothermic degradation peaks.

C O N T E N T S

	Page
CHAPTER 1	General Introduction
1.1	Introduction 1
1.1.1	Oxidation 3
1.1.2	Hydrogenation 5
1.1.3	Acid Transformation 6
1.1.4	Alkali Degradation 7
1.1.5	Fermentation 8
1.1.6	Tritylation Reaction 9
1.1.7	Methylation Reaction 11
1.1.8	Acylation Reaction 13
1.1.9	Sulfonylation Reaction 15
1.1.10	Acetalation Reaction 18
1.1.11	Methane Sulfonyl Chloride-N,N-dimethyl formamide Complex Reaction 21
1.1.12	Internal Displacement Reaction 23
1.1.13	Elimination Reaction 24
1.1.14	Chlorosulfonylation Reaction 25
1.1.15	Sucrose Epoxides 26
1.1.16	Nucleophilic Displacement Reactions of Sulfonic Esters of Sucrose 27
	References 32
CHAPTER 2	Sucrose Derivatives and Their Utility
2.1	Introduction 39
2.1.1	Part A 40
2.1.2	Part B 54
2.1.2.1	Sucrose Based Polyethers 55
2.1.2.2	Sucrose Based Polyesters 64

	<u>Page</u>	
4.2.2	Solubility and Chemical Resistance	131
4.2.3	Density Measurements	131
4.2.4	Viscosity Measurements	132
4.2.5	Infrared Spectra Studies	135
4.2.6	Proton Magnetic Resonance Studies	136
4.2.7	Elemental Analysis	137
4.3	Results and Discussion	137
4.3.1	Nature of Dibasic Acids and Physical State of Products	137
4.3.2	Hydroxyl and Acid Number	139
4.3.3	Solubility and Chemical Resistance Measurements	146
4.3.4	Intrinsic Viscosity	148
4.3.5	Density Measurements	154
4.3.6	Infrared Spectral Studies	157
4.3.7	Quantitative IR Studies	160
4.3.8	Quantitative PMR Studies	162
4.3.9	Elemental Analysis	165
	References	166
CHAPTER 5	Thermal Studies	
5.1	Introduction	168
5.2	Mechanism of Thermal Degradation of Carbohydrates	168
5.3	Experimental	173
5.3.1	Thermogravimetric Analysis	173
5.3.2	Differential Thermal Analysis	178

	<u>Page</u>	
5.4	Results and Discussion	178
5.4.1	Thermogravimetric Analysis	178
5.4.1.1	Effect of Acid Content of the Polymers on Thermal Stability	188
5.4.1.2	Effect of Intrinsic Viscosity on Thermal Stability	190
5.4.1.3	Effect of Atmosphere	191
5.4.1.4	Activation Energy	192
5.4.2	Differential Thermal Analysis	198
5.5	Investigation of the Reaction Products, Ti ₅ to Ti ₈ of Sucrose and Terephthaloyl Chloride Obtained by Interfacial Polycondensation	199
CHAPTER 6	Summary and Conclusion	204