THESIS ENTITLED

SYNTHESIS AND CHARACTERIZATION OF SOME POLYESTERS

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THESIS ENTITLED

SYNTHESIS AND CHARACTERISATION OF SOME POLYESTERS

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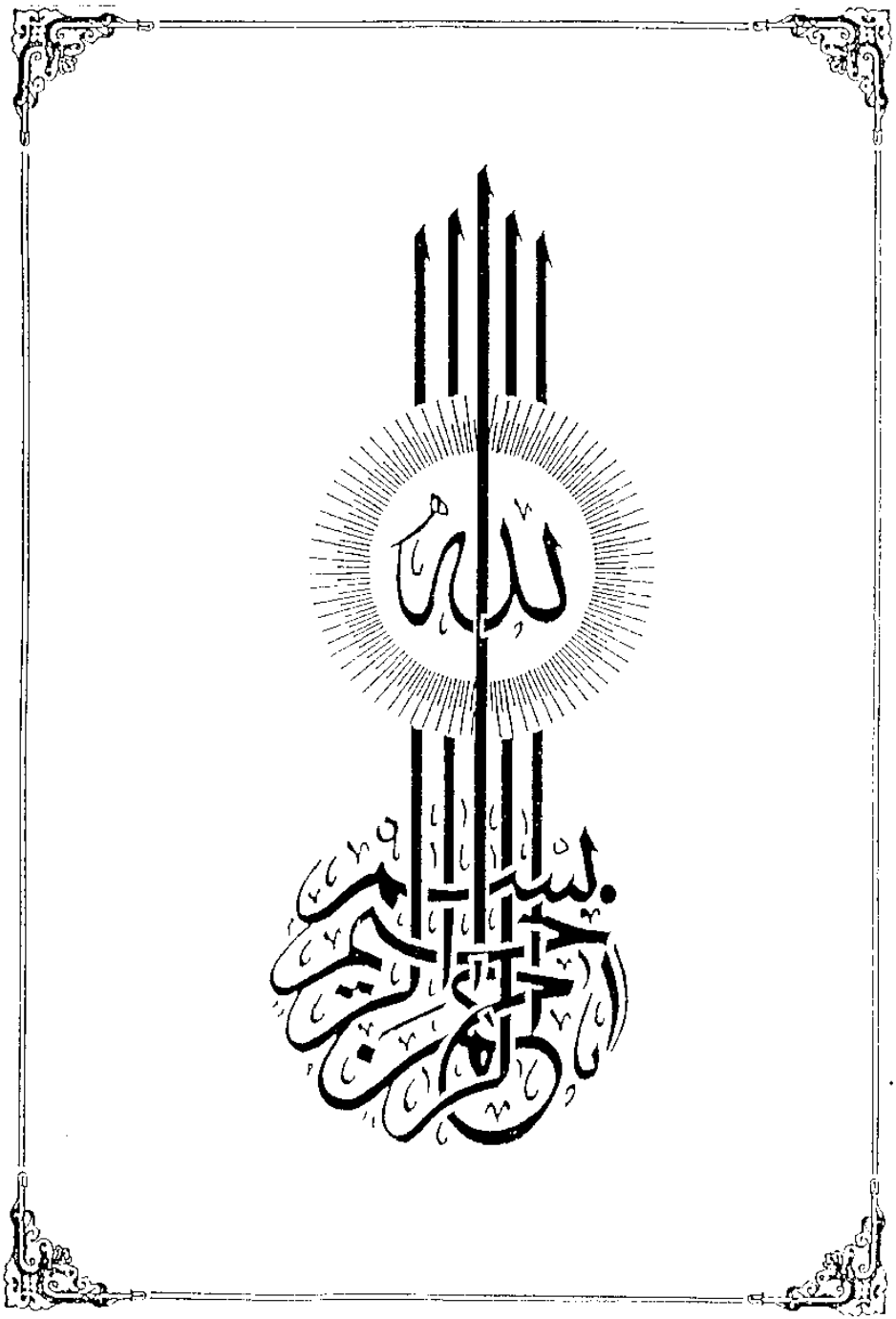

N O T E

Besides the work carried out in this thesis, the candidate has attended postgraduate courses in the following topics:

1. Physical Organic Chemistry.
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A C K N O W L E D G E M E N T

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SUMMARY IN ARABIC

S U M M A R Y

Unsaturated polyester resins were prepared by the ester interchange method between the two half esters of p-carbethoxy-maleananilic acid, p-carbethoxysuccinanilic acid with different saturated and unsaturated diols, namely, ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,6-hexanediol, and 1,4-butenediol. Moreover, copolymers were also prepared by the polyesterification of p-carbethoxymaleananilic acid, p-carbethoxysuccinanilic acid, maleic anhydride together with the above mentioned glycols. The prepared polyesters and copolymers were brown viscous resins, soluble in most organic solvents but insoluble in n-hexane and light petroleum.

The structure of the prepared resins was studied by means of infrared, ultraviolet and nuclear magnetic resonance spectroscopy. Viscosity measurements and molecular weight determinations provided further tools to their structure elucidation.

Curing of the prepared polyester resins and copolymers with styrene or methyl styrene monomers was attempted in

the presence of benzoyl peroxide as initiator. While all the copolymers resulted in insoluble products having network structures, only one polyester, namely the one prepared from p-carbethoxymaleananilic acid, p-carbethoxysuccinanilic acid and 1,6-hexane diol, gave a cured product. The other polyester resins failed to cure.

Evidence for the structure of the cured products was gained by subjecting them to hydrolytic decomposition in order to transform them into soluble products easy to be identified by physical tools, namely IR, UV, NMR spectra together with molecular weight determination.

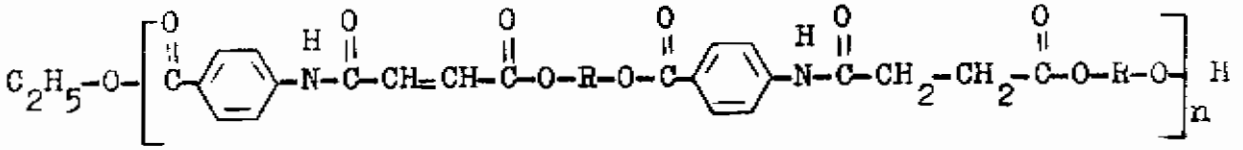
The cured copolymers prepared were tested as surface coating materials. Hardness and thickness of the films were measured. All cured films were not affected by cold water, hot water, 5% H_2SO_4, and 5% Na_2CO_3, but damaged by 5% NaOH at different time intervals.

AIM OF THE PRESENT WORK

In a previous work[25,26] p-carbethoxymaleananilic acid (I) was polymerized with different acids and glycols in order to prepare various polyesters having unsaturated backbones. Similarly, various polyester resins were prepared by the ester interchange method between p-carbethoxysuccinanilic acid (II) and different glycols, with or without maleic anhydride.

The previously mentioned polymers and copolymers were cured with styrene monomer to obtain polymers that were insoluble, infusable, and had net-work structures.

It was the aim of the present work to study the effect of mixing both the half esters (I) and (II) in 1:1 molar ratio on the physical and chemical properties of the formed polymers when (I) and (II) were condensed with various saturated and unsaturated glycols. It was of interest also to find out, whether or not both acids were present in the polyesters backbones in equal ratios. Thus, it was the aim of this work to determine whether polyester resins of the following structure were formed under the reaction conditions:



where R= $-CH_2-CH_2-$, $-CH_2CH_2-O-CH_2CH_2-$, $-\underset{CH_3}{CH}-CH_2-$, $-(CH_2)_6-$ and $-CH_2-CH=CH-CH_2-$.

Similarly, it was intended to copolymerize the previously cited half esters (I) and (II) with the same glycols previously used and maleic anhydride in order to built up highly extended unsaturated backbones that can be easily cured with styrene monomer in the presence of benzoyl peroxide as an initiator.

It was further intended to elucidate the structure of the prepared polyesters and copolymers by studying their infrared, electronic and n.m.r. spectra as well as by molecular weight determination.

It was also interesting to test the reactivity of the double bond present in the unsaturated backbone of the prepared polyester resins and copolymers towards styrene monomer in the presence of peroxide initiator to obtain cross-linked structures.

It was further hoped to obtain improved film properties

when the above cured polymers were used as surface coating materials as compared with those prepared using each half ester alone[25,26].

Knowledge on the structure of the cured polyesters was also one of the goals of the present work. Therefore, the hydrolytic decomposition was applied to the cured polymers, and the structure of hydrolytic products was studied by infrared, electronic and n.m.r. spectra, together with molecular weight determination.

CHAPTER I

C H A P T E R I

General Concepts Of Polymers

Polymers are macromolecules built up by linking together a large number of smaller molecules which are termed monomers; and the reactions by which they combine are termed polymerization reactions.

Carothers[1] defines polymerization as a reaction which is functionally capable of proceeding indefinitely. The structure of a polymer can be described in terms of the structural units, which are groups having two or more available bonding sites and are linked to one another through covalent bonds in the polymer molecule.

Types of Polymers

Polymers are classified into:

1. Linear Polymers:

They are polymers in which the carbon atoms are joined together as a continuous sequence in a chain.

$$X-R-R-R-R-R-Y \quad \text{or} \quad X-(R)_n-Y$$

where (R), the repeating unit, is a bivalent radical, (X)

and (Y) are functional groups capable of reacting with each other in a known fashion to form a new functional group; and (n) is the number of repeating units present in the polymer chain and is called the degree of polymerization (DP) which describes the molecular size.

Polyethylene and poly(ethylene adipate) may be taken as examples of linear polymers.

2. Branched Polymers[2]:

Branched polymer molecules are those in which there are side branches of linked monomer molecules protruding from various centeral branch points along the main polymer chain.

The presence of branching in a polymer usually have a large effect on many important polymer properties. It has been found that for a branched molecule, at least some of the units must be trivalent.

3. Net-Work Polymers:

Polymers may also have crosslinked or space net-work structures. These infusible and insoluble polymers are also called three-dimensional systems. Net-work polymers are also called thermosetting polymers.