CHAPTER-1

INTRODUCTION
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The rapidity of the all around developments in polymer science and technology and the unprecedented pace of applications necessitate fresh efforts in organising old and established thoughts, ideas, concepts, practices and updating them in the light of latest unfoldings. Today economically attractive raw materials and processes support the economy of many generic industries that are totally dependent on the synthetic macromolecules. Simultaneously, academic development took so fast that even 55 Journals devoted to polymer science around the globe have become shorts.

In order to study the relationship between the chemical structure and physical properties, the excellent field of polymer science was initiated by H. Staudinger[1], W.H. Carother[2] and propagated by a number of eminent scientists like P.J. Flory[3], R.W. Lenz[4] and M.P. Stevens[5].

The emerging areas of polymer science including synthesis of new monomers, initiators and polymers to meet the requirement of mankind. It is the basic cause of rapid growth of polymer industry, so much so that major percent of the chemists are involved in the synthesis and characterization of polymers. Amongst new polymers with specific properties are star polymers, liquid crystalline polymers, interpenetrating polymer network and polymers from terpenes.

[1]
Star Polymer

The nematic structure for Main Chain Liquid Crystalline Polymers
The terpenes generally do not homopolymerize due to steric hinderance\cite{6,7}, low stabilization energy between monomers and free radical transition state\cite{8}, excessive chain transfer reactions\cite{9} and termination or cyclization. As a result few publications, mostly devoted to bicyclic terpenes like α and β-pinene,\cite{10,12} acyclic and monocyclic monoterpenoid viz. isoprene\cite{13} and limonene,\cite{14}
are available in literature. However, dearth of literature is available on polymerization of terpenoids\textsuperscript{15-17}.

The terpenoids form a group of compounds, the majority of which occur in plant kingdom and terpenoids have been from other sources. The odour of flowers (rose, jasmine), roots (lemoncloves), leaves (mint, eucalyptus) and wood (sandalwood) of several plants, have been known to us since ancient times. The essential oils obtained by steam distillation or their parts have been widely used for perfumery, food flavouring and medicines, but very little was known about their chemical nature. Although some naturally occurring unsaturated hydrocarbon i.e. terpenes, in the form of homo-/co-/terpolymers with monomers other than terpenes have been investigated\textsuperscript{18-19}, it is because of their outstanding resistance to aging, thermal stability, colour, tack retention and adhesive properties. Therefore, polymers from terpenes have been used in a great number of commercial applications. These are particularly useful in the manufacture of adhesives, coatings, sizing materials, rubber compounding, floor wax polishes, printing inks, chewing gum base, paints, varnishes, plasticizers, concrete curing, food packaging, manufacture of containers which come in contact with food for human consumption.

**Group Transfer Polymerization:**

The silicon mediated sequential Michael addition of $\alpha,\beta$-unsaturated esters, amides and nitriles has been termed as
Group transfer polymerization. It can be summarised as below:

\[
\begin{align*}
R & \rightarrow Si \rightarrow R + Nu \\
R & \rightarrow Si \rightarrow R + Nu \\
R & \rightarrow Si \rightarrow R + Nu \\
R & \rightarrow Si \rightarrow R + Nu
\end{align*}
\]

1-methoxy-1-(trimethylsiloxy) -2- methyl-1-propene
Pentacoordinate species
Hypervalent silicon intermediate
5

Where, \( R = CH_3 \)
\( Nu = \text{Nucleophilic catalyst e.g. HF}_2 \)

Star Polymers:

Star polymers consist of multiple linear chains linked together at one end of each chain by a junction point. These are nano-scale ordered materials which are of interest because of their spatial shapes and low viscosity compared with that of linear polymers with similar molecular weights. Star polymer are three dimensional
hyperbranched structures in which linear arms of the same or different molecular weights emanates from a central core. The existence of numerous functional groups in a small volume makes these polymers important for use in biological and pharmaceutical applications. The structure of a star polymer is as follows.

Plasma Polymerization:

Plasma polymerization is a thin film forming process where thin films deposit directly on the surface of the substrate. In this process the growth of low molecular weight molecules (monomers) into high molecular weight molecules (polymers) occurs with assistance of plasma energy, which involves activated electrons, ions and radicals.

Plasma polymers are amorphous, hard tough and insoluble in organic solvents and resistant to high temperature. These
unique properties result from the chemical structure of plasma polymer chains, which results highly crosslinked and branched polymers.

Interpenetrating Polymer Network:

The dynamic mechanical properties of a macromolecular system may be improved significantly by interpenetrating complexation of hybrid binders, whose use makes it possible to achieve much more complex combination of different polymer(s) structure, structural state in composite materials are interpenetrating polymer network (IPN’s). The name IPN was laid down by Miller in 1960. An interpenetrating polymer is defined as an intimate combination of two crosslinked polymers, at least one of them is synthesized or crosslinked in the immediate presence of other polymer.
synthesis of IPN forms an important category of polymer science which can yield a material with properties quite different from its components.

A+B initiator

monomer A,B

initiator

A+B

cross linker

oxidizing agent

flexible crosslinked network

In situ polymerization

conducting monomer

Liquid Crystalline Polymers:

During the last two decades a new class of polymeric materials have been developed which received a great deal of attention from both industry and academica. These materials are called liquid crystalline polymers. In the liquid state, either as a solution (lyotropic) of melt (thermotropic), these lie between the boundaries of solid crystals and isotropic liquids. The polymeric state is also referred to as mesomorphic structure and as mesophase.
Living Radical Polymerization:

One of the main goals in modern synthetic polymer chemistry is to prepare polymers with controlled molecular weight and well-defined architecture. The living free radical polymerization (LFRP) is one of the most important industrial processes to prepare such polymers. The polymeric material synthesized via LRP technique has gained much attention because of their mild reaction conditions, compatibility with a wide range of monomers, and high tolerance to impurities, functional groups, and additives.