

Module 16 Polymers

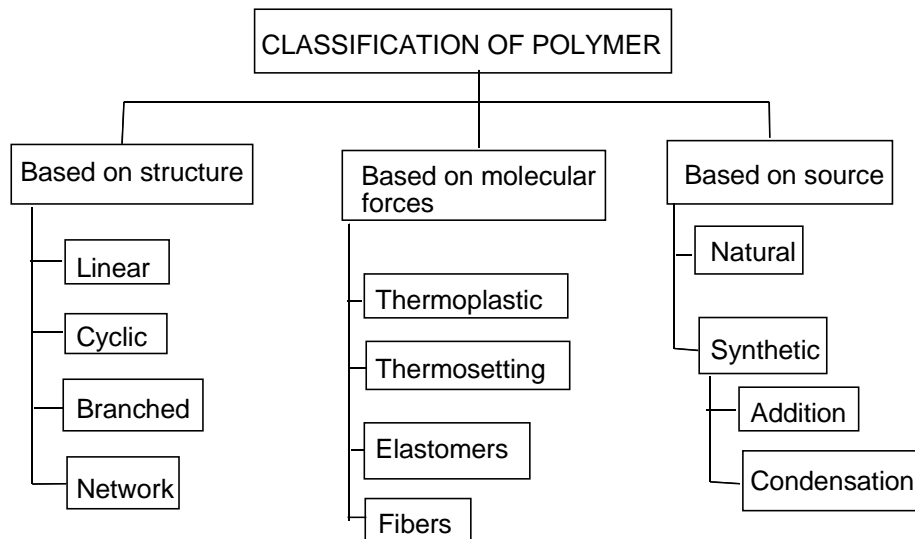
Lecture 39 Polymers I

16.1 Introduction

A polymer is a macromolecule, made up of many smaller repeating units called monomer. Polymers have high molecular weight in the range of several thousand or even higher. The first synthetic organic polymer polyvinylchloride was synthesized in 1838 by accidentally. Later, polystyrene was discovered in 1839.

16.2 Classification

Polymers can be classified into a number of ways which are described below.



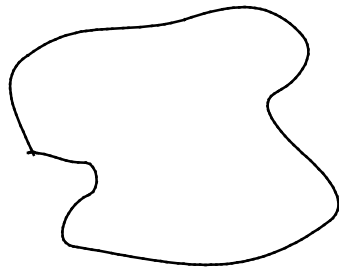
Polymers can be divided into four types depending on its skeletal structure.

- A linear polymer is represented by a chain with two ends.
- A cyclic polymer have no chain ends and show properties that are entirely different from their linear counterparts.

linear

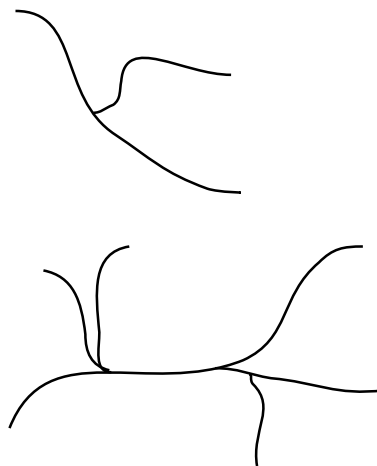


cyclic



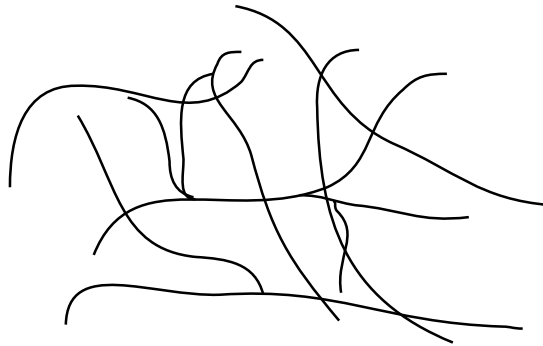
- Branched polymers have side chains, or branches, of significant length which are bonded to the main chain at branch points, and are characterized in terms of the number and size of the branches.

branched



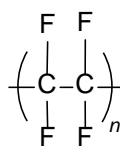
- Network polymer or cross-linked polymer have three dimensional structures in which each chain is connected to all others by a sequence of junction points and other chains. But it does not contain any main chain when compare with branched polymer.

network



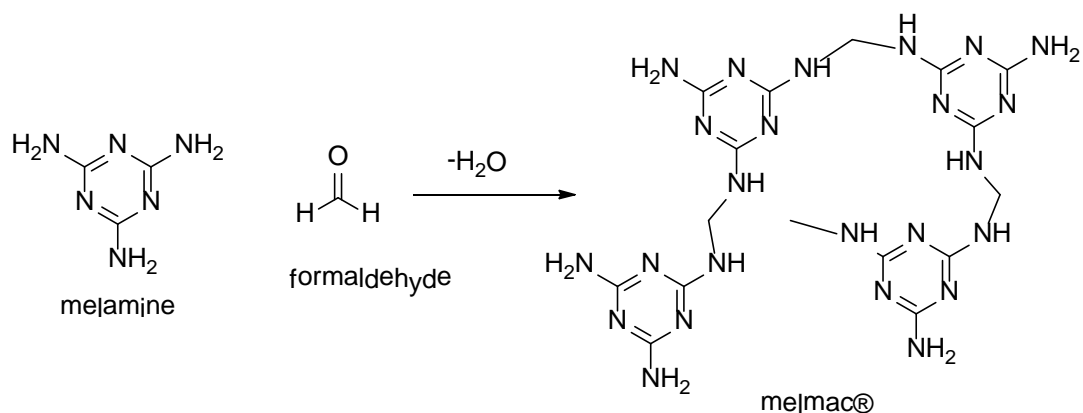
Similarly, polymers can be classified into four categories based on the forces of attraction between polymer chains are thermoplastic polymers, thermosetting polymers and elastomers.

Thermoplastic Polymers: The individual chains of thermoplastic polymer are held together by van der Waals forces. They are strong if the polymer chains are lined up in an ordered, closely packed array. This region is called crystallites and the other where polymer chains are oriented randomly is called amorphous. Thermoplastic polymers have both ordered crystalline regions and amorphous noncrystalline regions. Thermoplastic polymers are hard at room temperature, but become soft when heated, because on heating individual polymer chains slip from one another. Polyethylene, polystyrene, polypropene and teflon are some examples for thermoplastic polymer.



Teflon

Thermosetting Polymers: The greater the degree of cross-linking makes the polymer more rigid. Such cross-linked polymers are called thermosetting polymers. Thermosetting polymers are generally stronger than thermoplastic polymers due to strong covalent linkage (cross-linking) between polymer chains not by weak intermolecular van der Waals forces. They are more brittle in nature and their shape is permanent. Once it is hardened they cannot be recycled. Melmac®, a highly cross-linked thermosetting polymer of melamine and formaldehyde, used to make lightweight dishes. Bakelite and polyurethanes are examples for thermosetting polymers.



Elastomers: An elastomer is a randomly oriented amorphous polymer, which stretches and then reverts back to its original shape. To avoid slipping of polymer chains it must have some cross-linking. When elastomers are stretched, the random chains stretch out where as the van der Waals forces are not strong enough to maintain them in that arrangement and retains its original shape when the stress is removed. Rubber is an example of an elastomer.

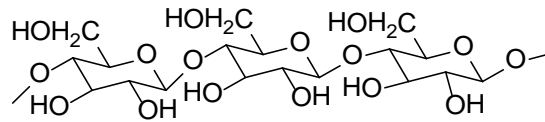
Fibers: These are thread like polymers which can be used as fabrics. The strong intermolecular forces like hydrogen bond provide high tensile strength and high modulus to fibers. A few examples are cotton, wool, silk, nylon etc.

Generally, polymers can be divided into two broad groups depending on the source, either natural polymers or synthetic polymers.

16.3 Natural Polymers

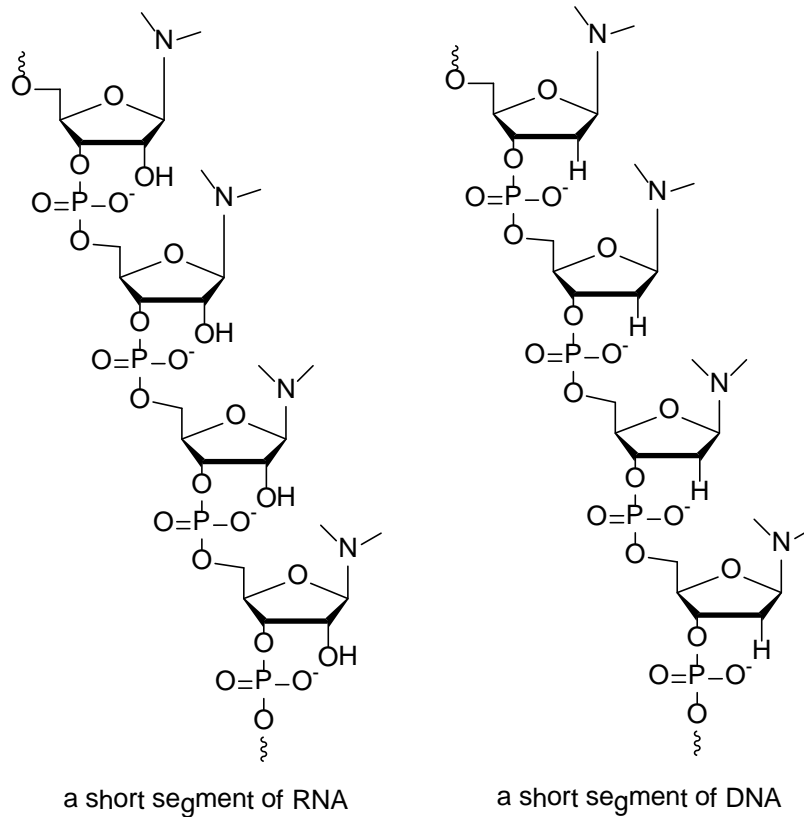
Polymers are naturally available. A few examples are:

Polysaccharides: Polysaccharides are important class of biopolymers which are made up of long chains of monosaccharide units bound together by glycosidic bonds. Polysaccharides contain more than ten monosaccharide units. Starch and glycogen are very common examples for storage polysaccharides. Similarly, cellulose and chitin are examples for structural polysaccharides.



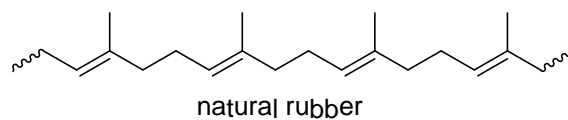
three subunits of cellulose

Nucleic Acids: Nucleic acids, such as DNA (deoxyribonucleic acid) and RNA (ribonucleic acid), are made from nucleotide monomers. Nucleic acids are found in all living things, where they function in encoding, transmitting and expressing genetic information.



Proteins: Proteins are large biological molecules, made up of the smallest units called α -amino acids. They are building blocks of plant and animal cells. Many proteins are enzymes that catalyze biochemical reactions and are essential to metabolic functions.

Natural Rubber: Natural rubber is the polymer of isoprene. This is mainly harvested as a sticky milky colloidal form called latex from the bark of the rubber tree.

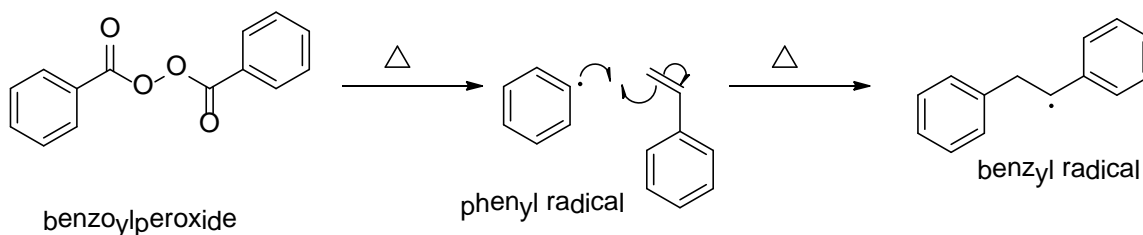


16.4 Synthetic Polymers

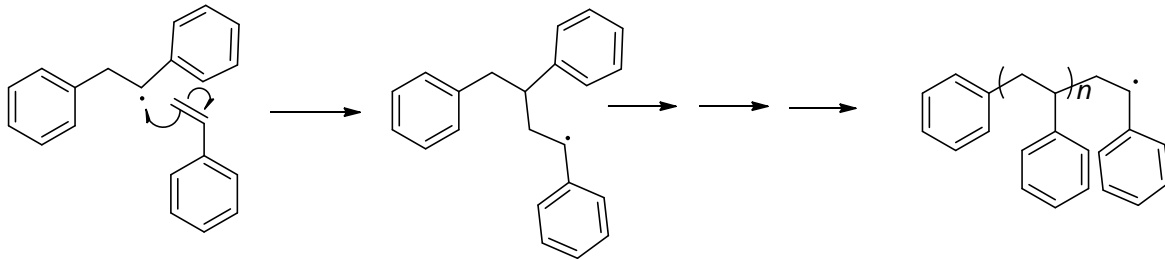
The polymers which are synthesized in the laboratory are called as synthetic polymers, based on the method of its preparation they can be further classified into addition polymers and condensation polymers.

Addition polymers: Addition polymers are formed by the sequential addition of the monomer units with the help of a reactive intermediate such as free radicals, cation or anions without loss of small molecules. The addition polymerization generally involves three steps called initiation, propagation and termination. These steps apply to all types of addition polymerization such as free-radical, cation and anion. In this process alkenes are typically used as monomers and polymerization results by successive additions across the double bonds.

- Radical polymerization results when a suitable alkene is heated with a radical initiator.
- *Initiation step:* On heating the initiator molecule decomposes into a radical which combines with the monomer and forms a new radical for the chain propagation.

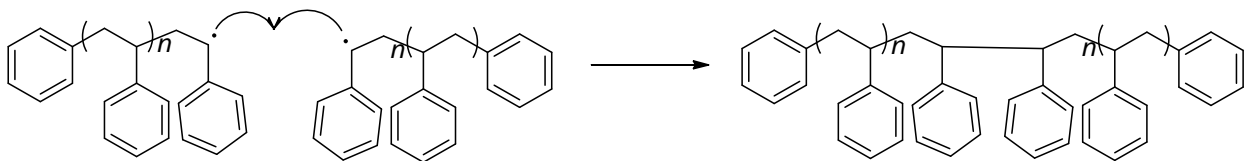


- *Propagation step:* The formed radical reacts with another monomer and generate a new radical which propagates the chain. The chain propagation process determines the length of a polymer chain.

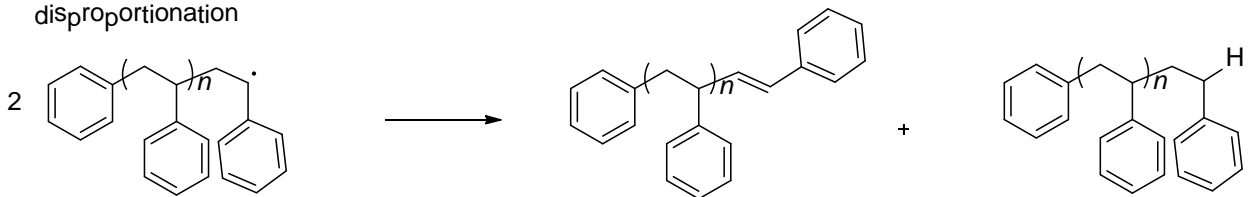


- *Termination step:* There are three ways to terminate the propagating chain either by coupling with another monomer radical or by disproportionation reaction or by reaction with an impurity (such as oxygen).

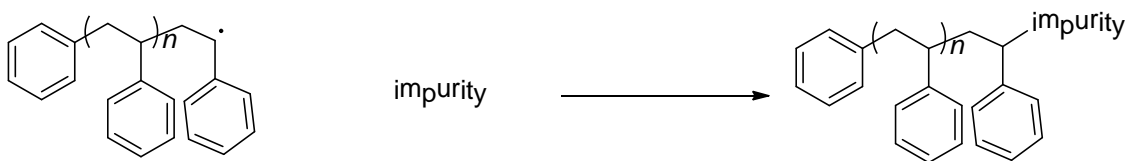
chain combination



disproportionation

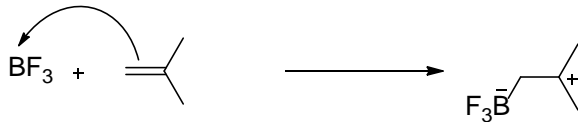


reaction with an impurity

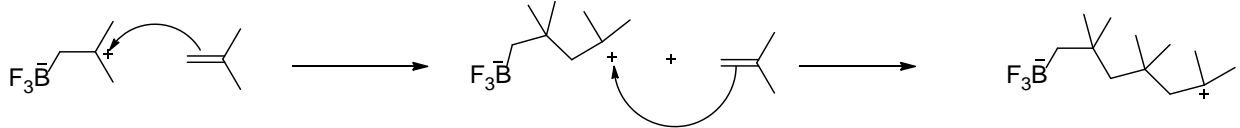


- In cationic polymerization, a cation intermediate is generated by the addition of a Lewis acid such as BF_3 , AlCl_3 , etc. with the monomer typically alkene. The cation formed in the initiation step reacts with another monomer and generate a new cation, this process is repeated until chain termination occurs.

initiation



propagation



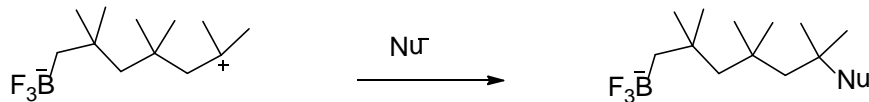
- Chain propagation can be affected by three ways either by loss of a proton or by addition of a nucleophile or by reacting with the solvent molecule.

termination

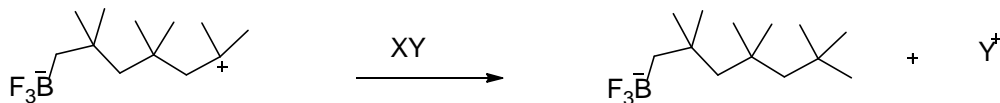
loss of a proton



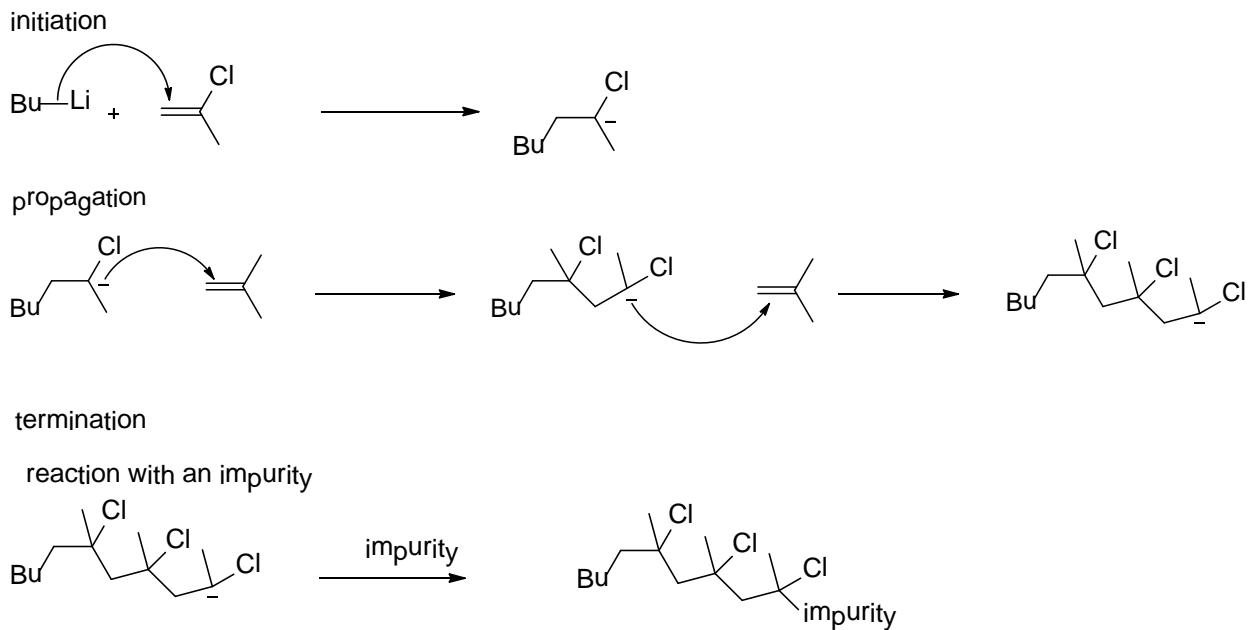
reaction with a nucleophile



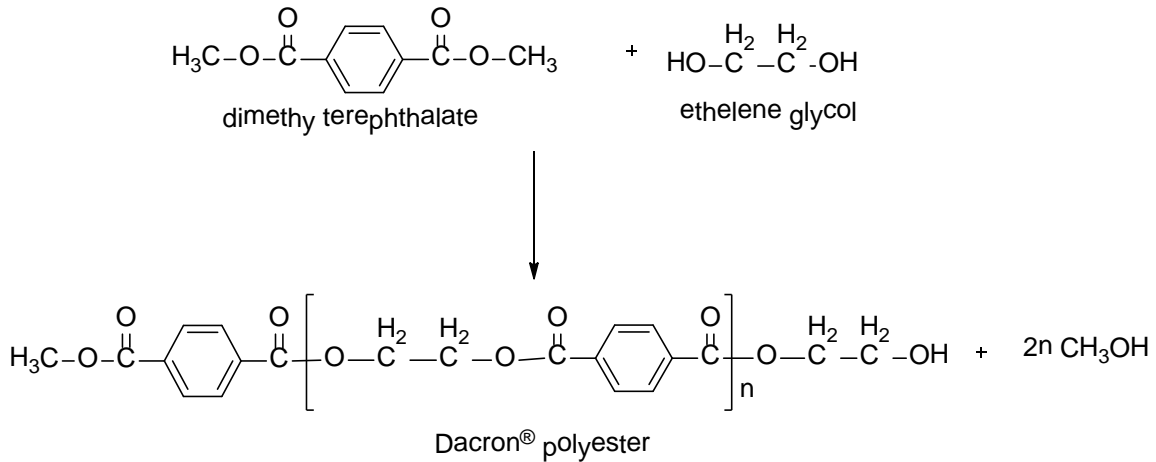
chain transfer reaction with the solvent



- Anionic polymerization occurs by the addition of a nucleophile initiator with the monomer alkene and generates a new anions, this process occurs only when the nucleophilicity of the initiator nucleophiles are strong enough to attack the electron rich olefins. Similarly, if electron withdrawing substituents are attached to the olefin bond increases the rate of addition. Here the chain propagation step was terminated by reaction of generated nucleophiles with impurity or solvent molecules.



Condensation Polymers: This type of polymers is generated by the condensation of two monomer units with the loss of small molecules such as H₂O, HCl, and NH₃ etc. Here the monomer units must have two functional groups in order to condensation reaction took place. Dacron[®], nylon 6 and nylon 66 are few examples for condensation polymers.

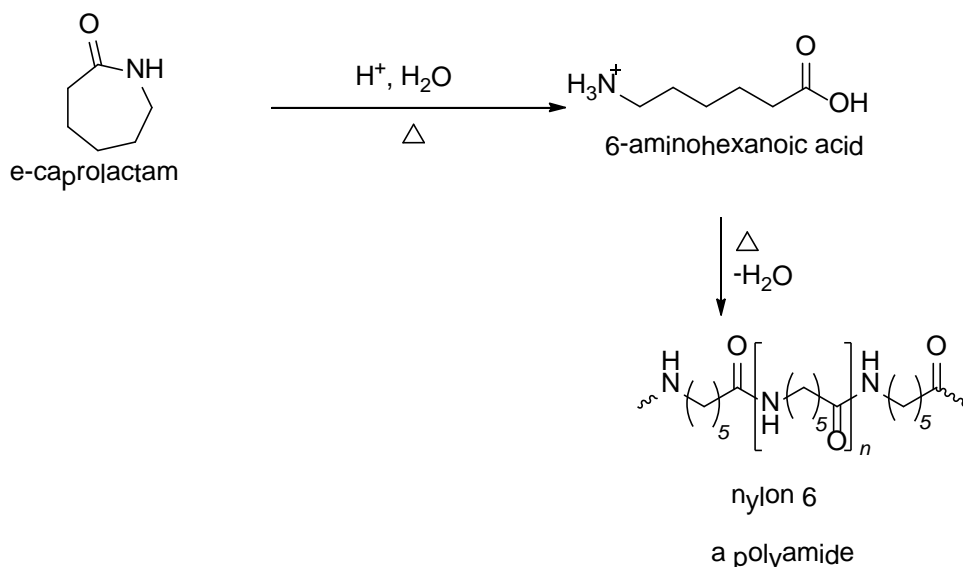


Copolymer: If the polymer chain is formed from only one type of monomer units are called homopolymers. Alternatively, two or more different monomer units can combine to form a polymer chain is called copolymers.

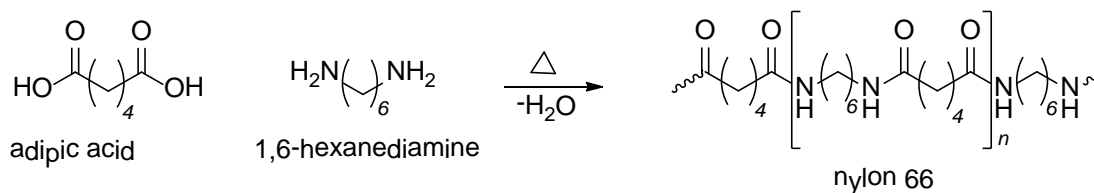
an alternating copolymer	ABABABABABABABABABABABAB
a block copolymer	AAAABBBBAAAABBBBAAAABBBB
a random copolymer	AABABABBAABAAABBAABABBBA
a graft copolymer	AAAAAAAAAAAAAAAAAAAAAAAAAA B B B B B B B B B B B B B B B B B B B B B B B B

There are four types of copolymers are known. First, alternate arrangement of monomer units results alternating copolymer. Secondly, block arrangement of monomer units result block copolymers. Thirdly, a random arrangement of monomer units results random copolymers and finally, a graft copolymers results by one type of monomer units are arranged at the branches of the chain and the another type of monomer units still reside at the main chain.

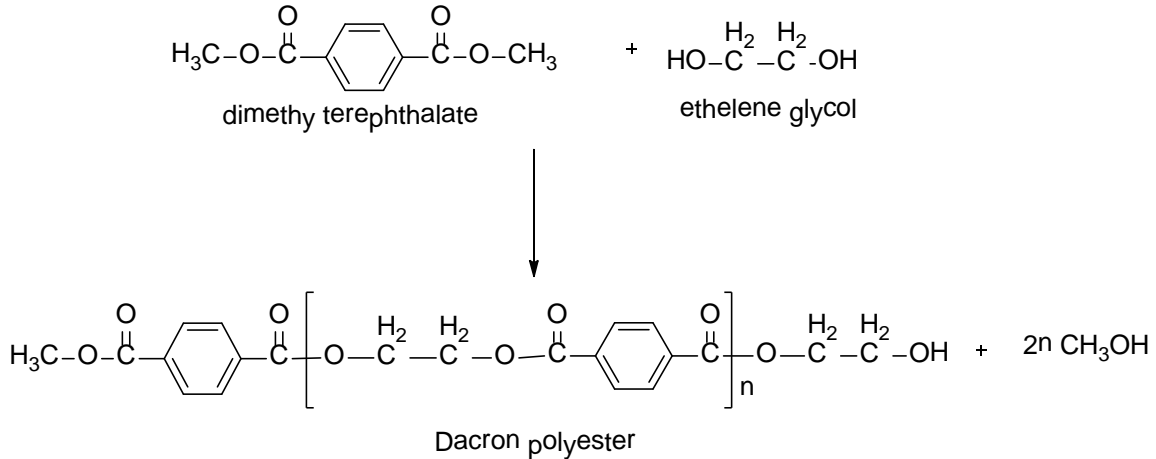
Polyamides: This type of polymers is formed by the result of generation of amide bonds in the polymerization reaction. Nylon 6 and nylon 66 are important examples for this type of polymers nylon 6 is synthesized from ϵ -caprolactam, which on heating decomposes into 6-aminohexanoic acid that polymerizes into nylon 6. Here the number 6 represents the number of carbon atoms present in the monomer unit.



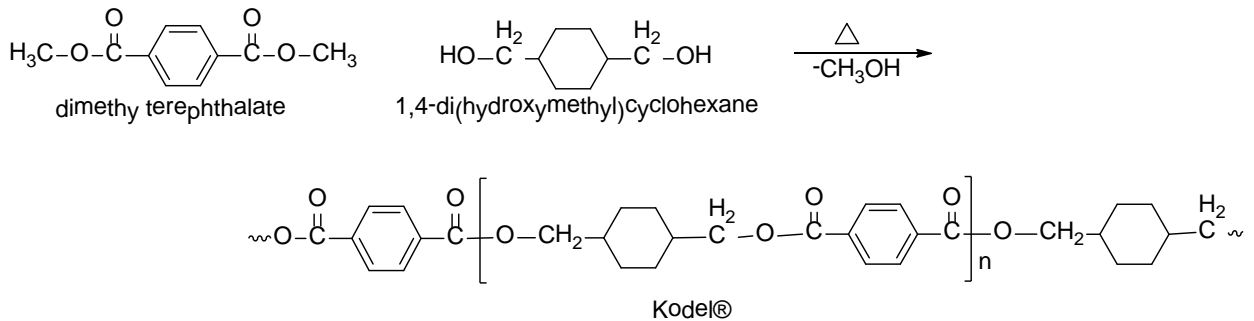
Nylon 66 is produced by the condensation reaction between two monomer units adipic acid and 1,6-hexanediamine in the presence of heat. This is formed from a six-carbon diacid and a six-carbon diamine.



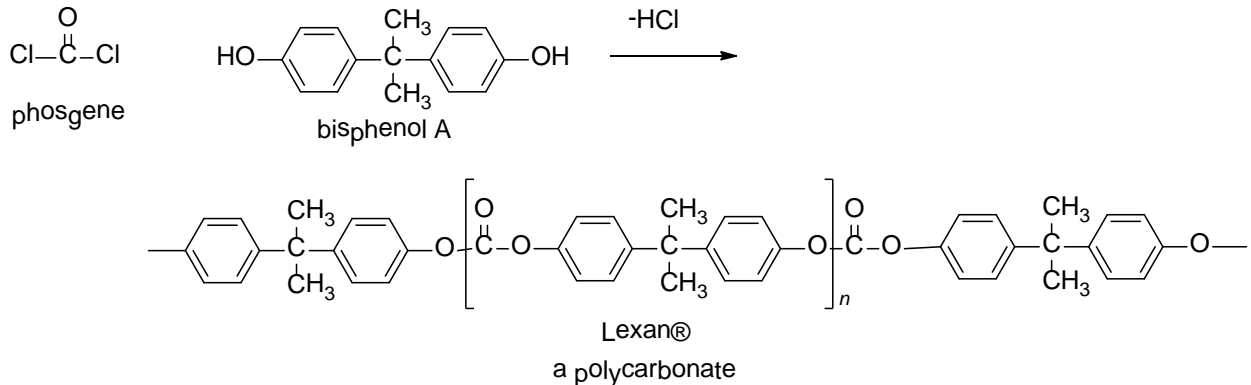
Polyesters: This type of polymers is generated by the result of formation of ester bonds in the polymer chain by the condensation reaction between two monomer units. Dacron® is a well-known polyester, synthesized by the transesterification of dimethyl terephthalate with ethylene glycol.



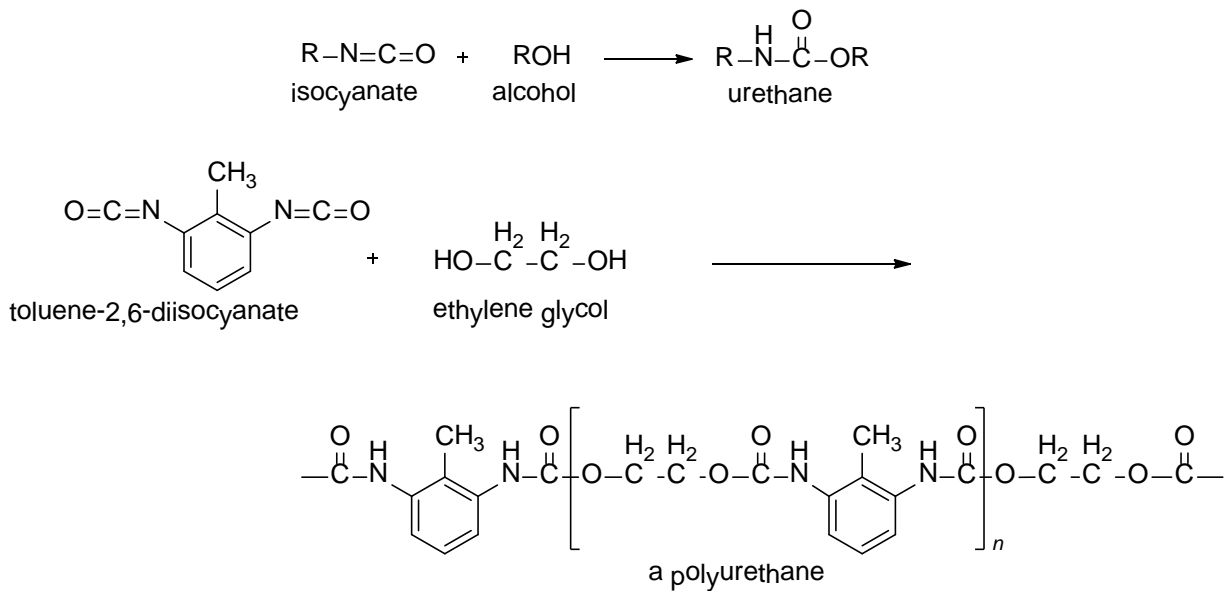
Similarly, trans esterification of dimethyl terephthalate with 1,4-di(hydroxymethyl)cyclohexane results Kodel® polyester.



Polycarbonates: This is an example for condensation of step-growth polymer. Here the polymer chain is linked together by carbonate bonds. Lexan®, a polycarbonate formed by the condensation reaction between the two monomers phosgene and bisphenol A. This is used for manufacturing bulletproof windows.



Polyurethane: A carbamate functional group is synthesized by the addition reaction of an alcohol with an isocyanate molecule. This is also called as urethane. If a polymer chain is linked together by urethane bonds are called as polyurethane. Typically, polyurethanes are prepared by the addition reaction of diol monomers with diisocyanate monomers. Polyurethane in the form of foams has been used for furniture stuffing, carpet backings and insulations.



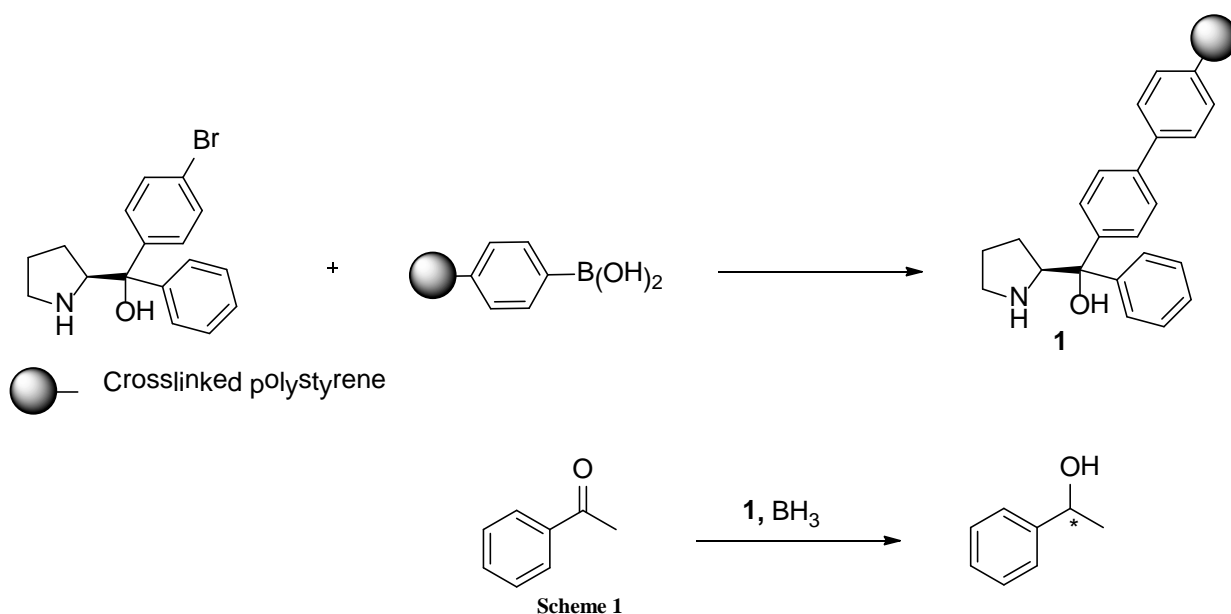
Module 16 Polymers

Lecture 40 Polymers II

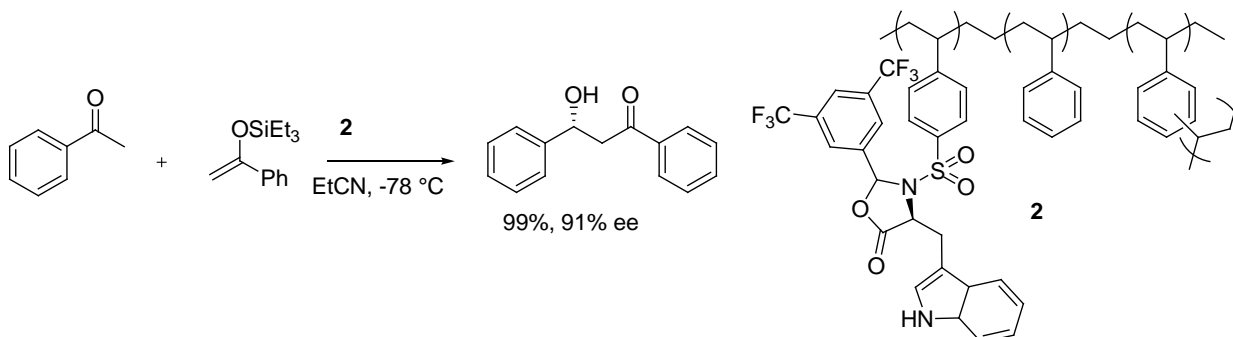
16.5 Application of Synthetic Polymers in Catalysis

Recently, polymer supported catalysts have received much attention in organic synthesis. The polymer support provides potential advantages such as easy separation and recovery of the expensive catalyst from the reaction mixture by simple filtration and allows it for subsequent reuse. The reduced toxicity and odor of polymer supported species are another advantage over conventional solution-phase reactions. Typically, polymer supported catalyst show higher activity as compared with the monomer catalyst; this is due to the increase in the number of reactive centers in the polymer catalysts. Generally Lewis acids can be immobilized to polymer support by covalent bonding or ionic bonding or coordination of polymeric ligands with metal species.

Hodge and coworkers have synthesized polymer supported oxazaborolidines with α,α -diaryl- β -aminoalcohol by Suzuki coupling of α,α -diphenyl-L-prolinol derivatives with cross-linked polystyrene containing phenylboronic acid residue.^{1,2} This supported catalyst shows high level of enantioselectivity up to 97% ee for the reduction of ketone to alcohol (Scheme 1).

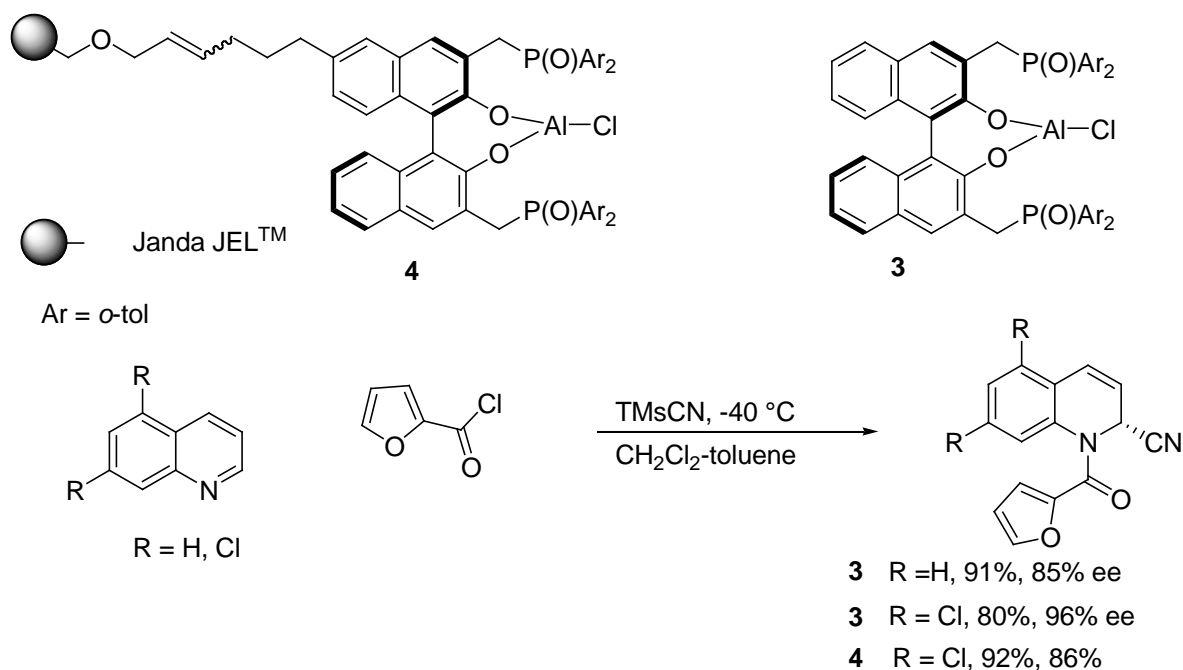


Itsuno et al. has reported cross-linked polymer supported chiral oxazaborolidinone catalyst for Mukiyama-aldol type reaction between aldehyde and silyl enol ether that provided β -hydroxyketone in >90% ee (Scheme 2). Further, this catalyst was used for asymmetric Mannich reaction and asymmetric allylation reaction.³



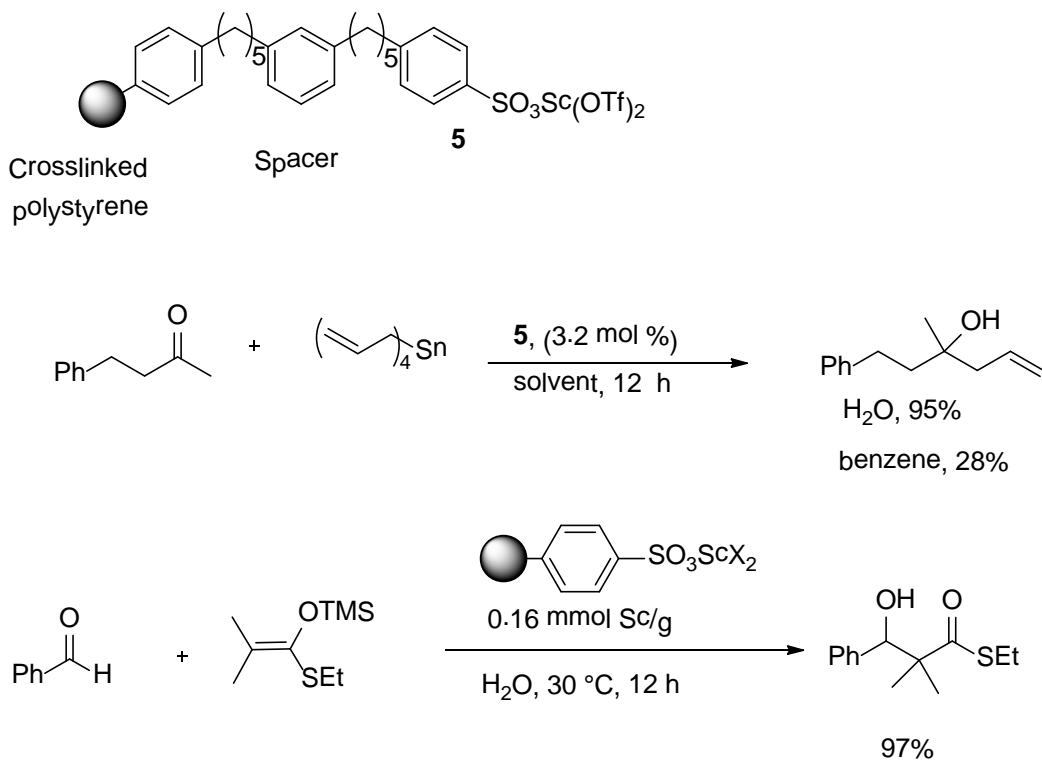
Scheme 2

Shibasaki and coworkers have developed a bifunctional chiral catalyst consisting Lewis acid (aluminium metal) and the Lewis base (phosphine oxide), which was successfully applied to asymmetric Reisser-type reaction of trimethylsilylcyanide with quinolone and 2-furoyl chloride (Scheme 3). This catalyst afforded high activity and nearly similar enantioselectivity as compared with the monomer.^{4,5}



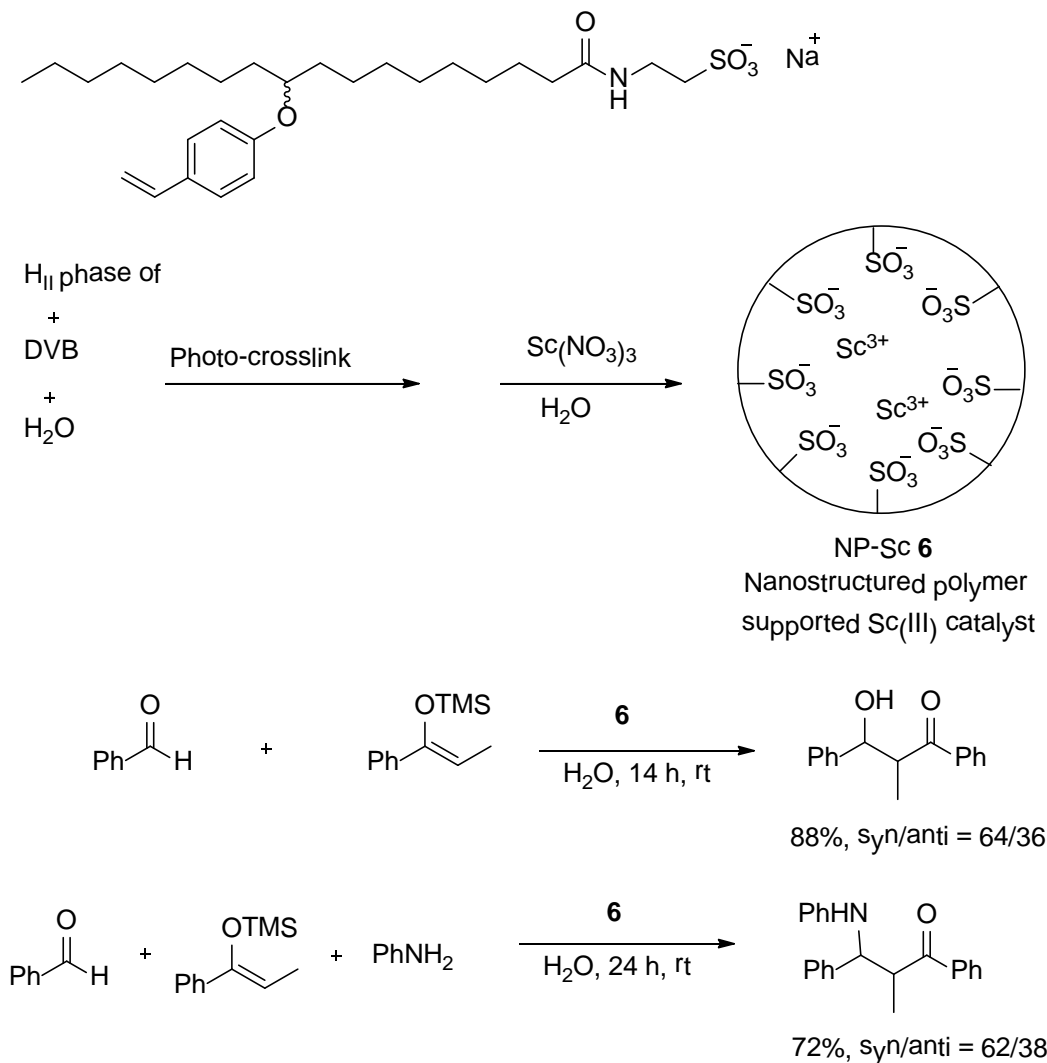
Scheme 3

Kobayashi et al. has developed hydrophobic polymer supported scandium catalyst for allylation reaction of ketone with tetra-allyltin in water (Scheme 4).⁶ The same catalyst **5** showed high activity in Mukaiyama-aldol reaction also and the reactions proceeded much faster in water than in other organic solvents.⁷



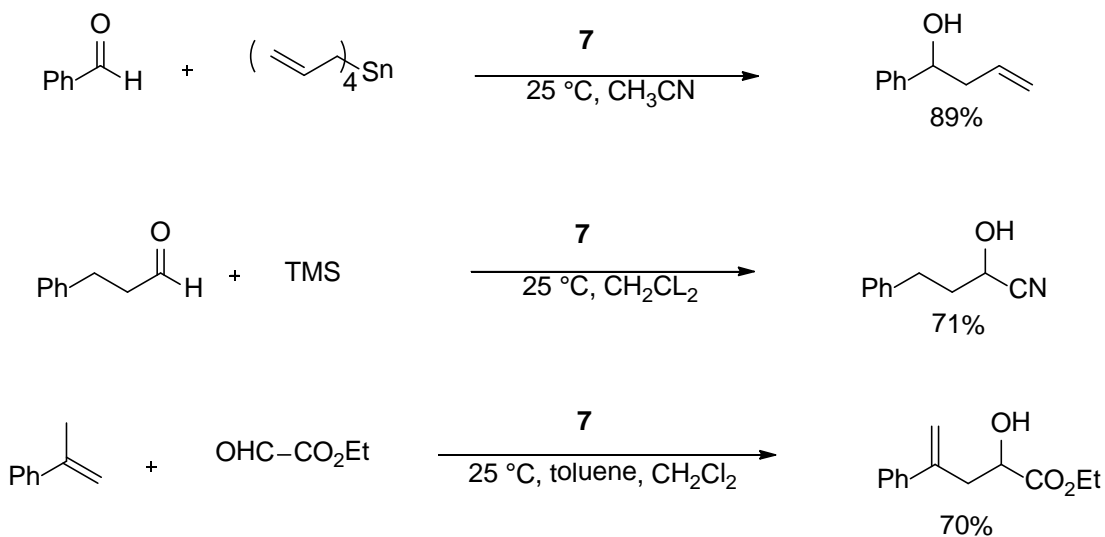
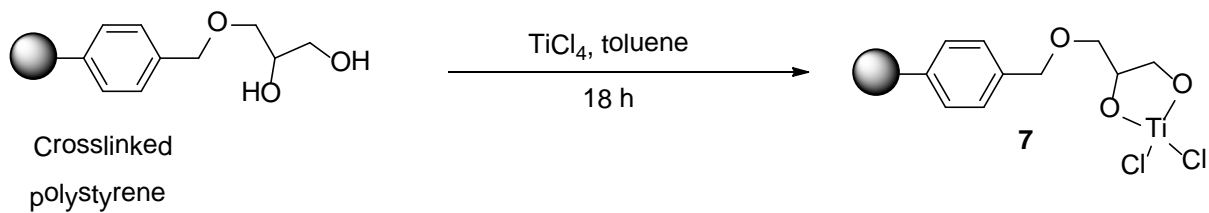
Scheme 4

Nanostructured polymer supported Sc(III) catalyst was prepared by cross-linking inverted hexagona (H_{II}) monomer containing sodium sulfonate head group with divinylbenzene, followed by exchanging sodium with scandium(III) nitrate (Scheme 5).⁸ This catalyst was tested for Mukiyama aldol and Mannich type reactions.



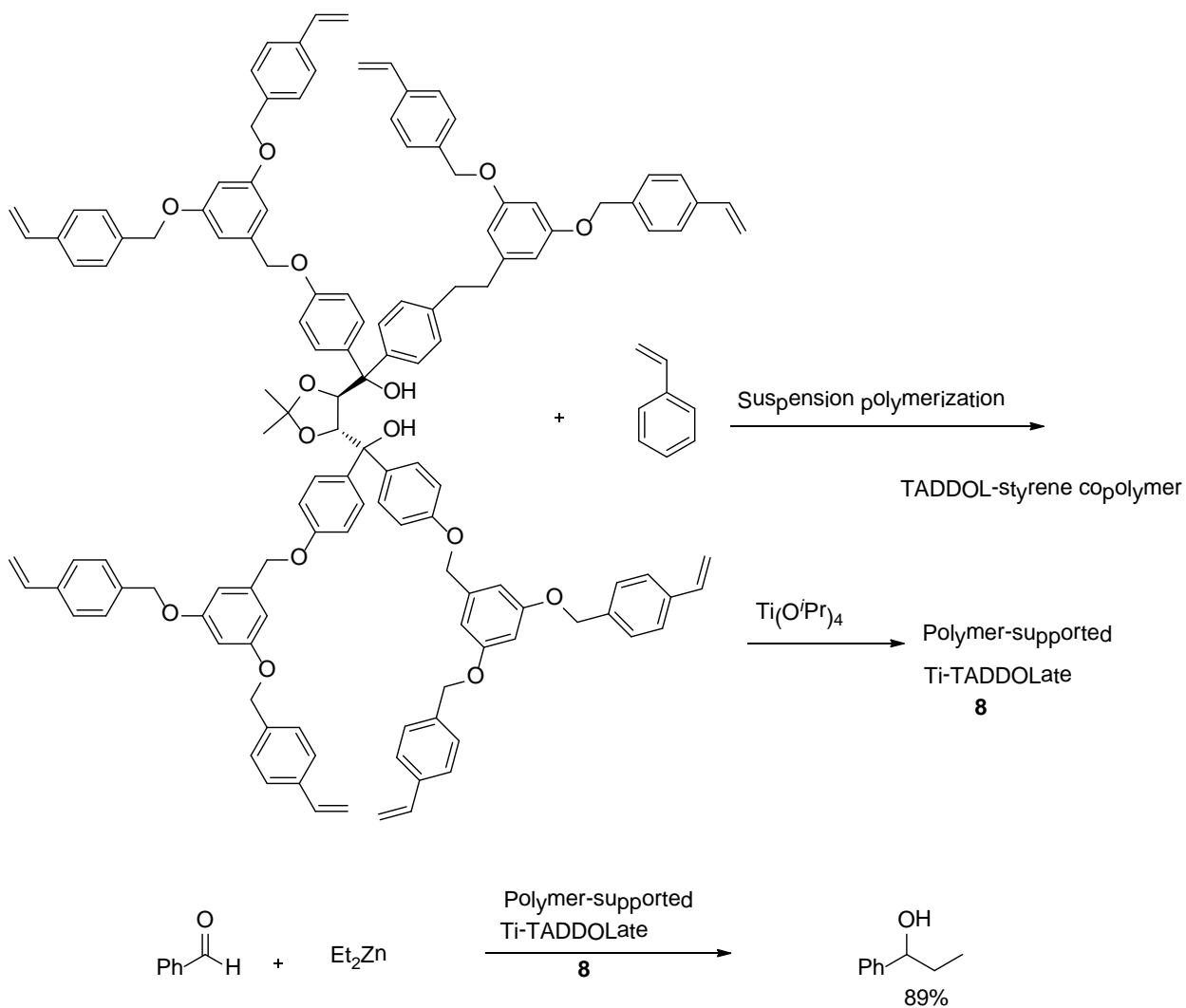
Scheme 5

Polymer supported Ti(IV) catalyst was explored for some carbon-carbon bond forming reactions including allylation, cyanation and ene reactions (Scheme 6).⁹



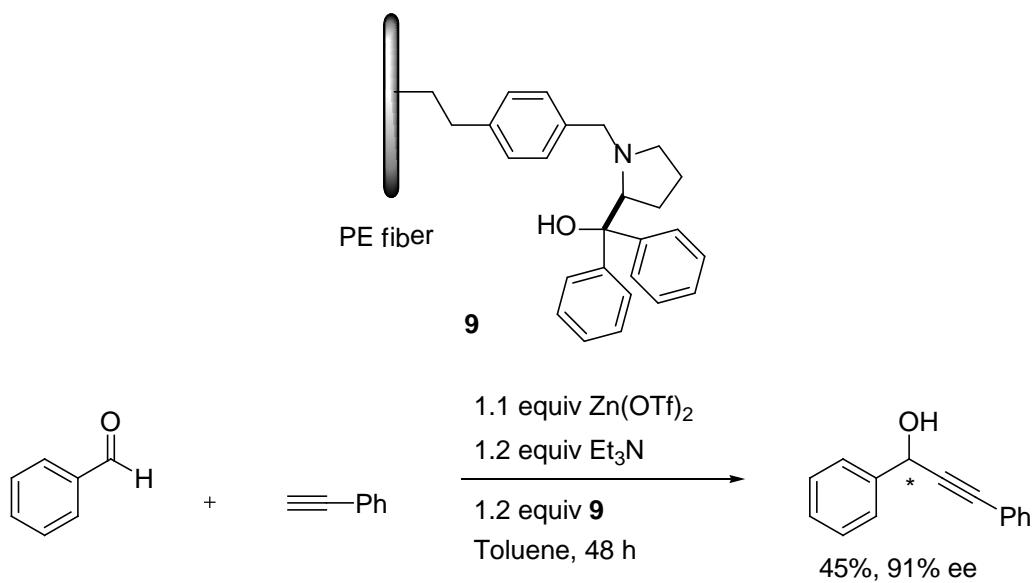
Scheme 6

Seebach and co-workers have developed polymer supported Ti-TADDOLate for enantioselective diethyl zinc addition to aldehydes.¹⁰ It showed high activity as well as enantioselectivity (Scheme 7).



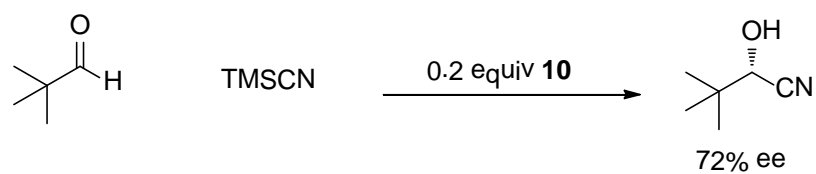
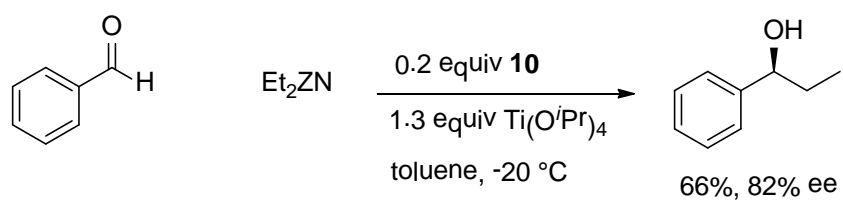
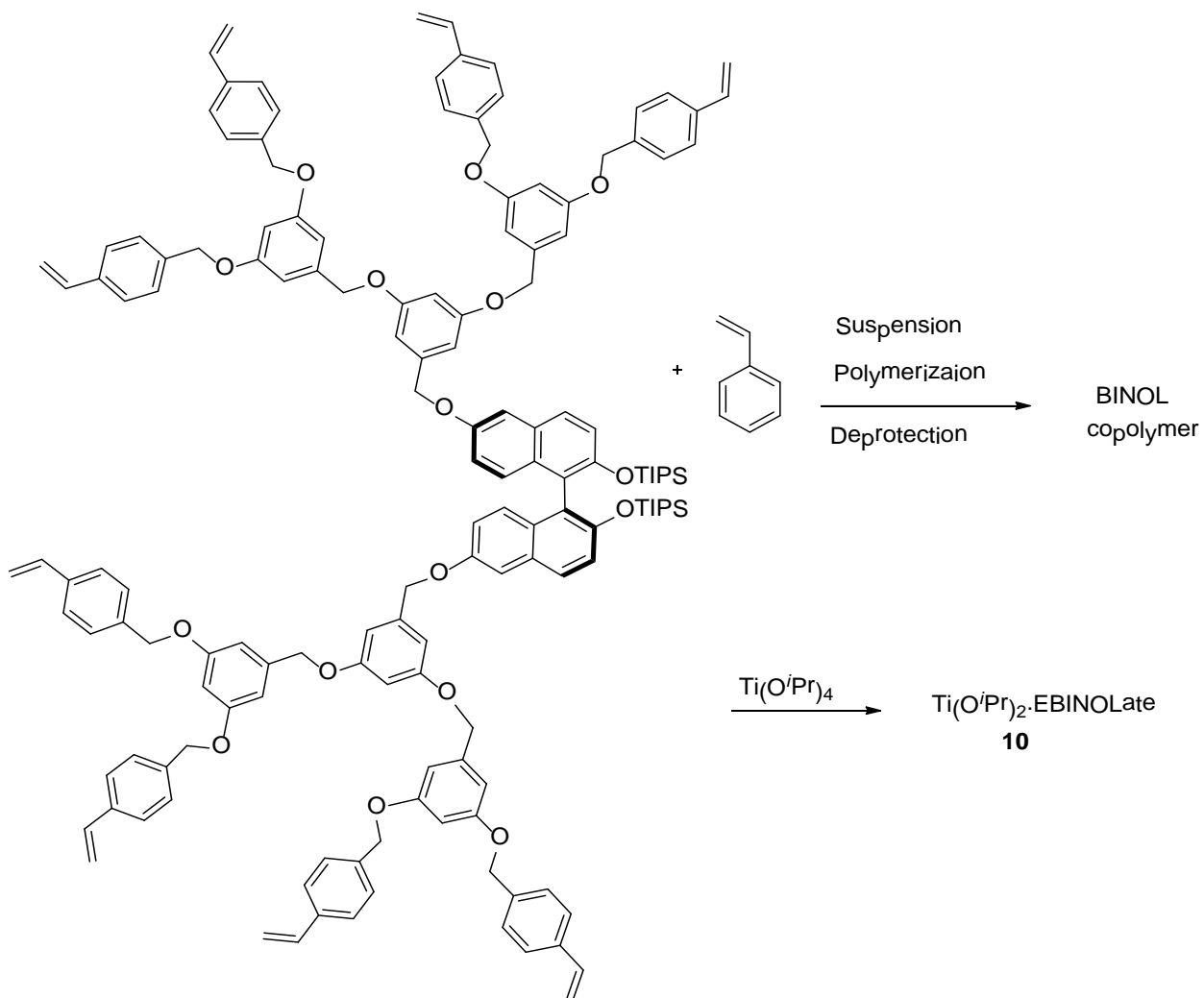
Chiral amino alcohol immobilized polyethylene (PE) fibers has been synthesized by electron beam induced perirradiation graft copolymerization method (Scheme 8).¹¹ This

more stable fibrous catalyst was used in phenylacetylene addition to benzaldehyde with $\text{Zn}(\text{OTf})_2$.



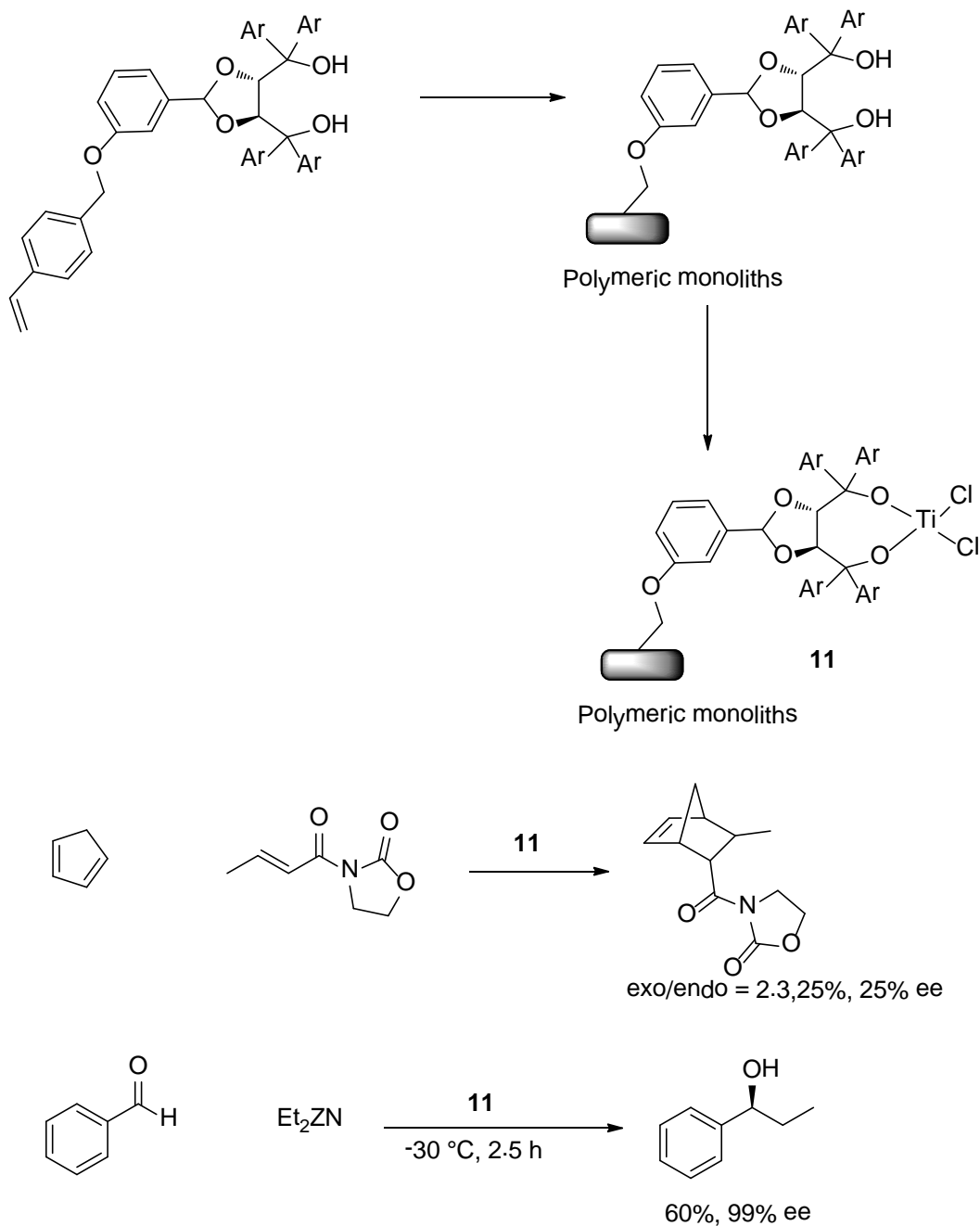
Scheme 8

Cross-linked polymer supported $\text{Ti}(\text{O}i\text{Pr})_2$ BINOLate complex was reported for enantioselective diethyl zinc and trimethylsilyl cyanide addition reaction with aldehydes (Scheme 9).¹²



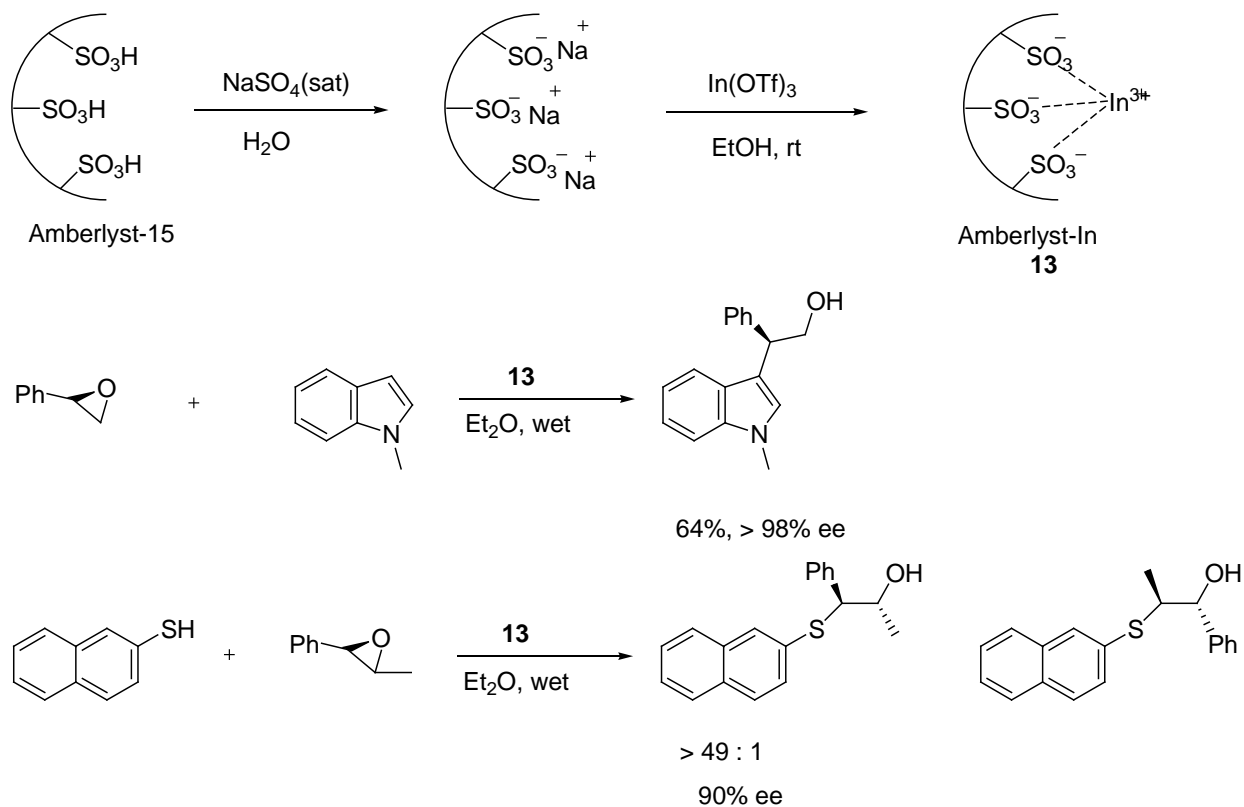
Scheme 9

Polymeric monolith containing TI-TADDOLate has been synthesized by thermally induced radical solution polymerization of a monomeric mixture containing TADDOL monomer, styrene and divinylbenzene, using azobisisobutyronitril (AIBN) as the radical initiator (Scheme 10). This catalyst was used for Diels-Alder reaction and diethyl zinc addition to benzaldehyde.¹³



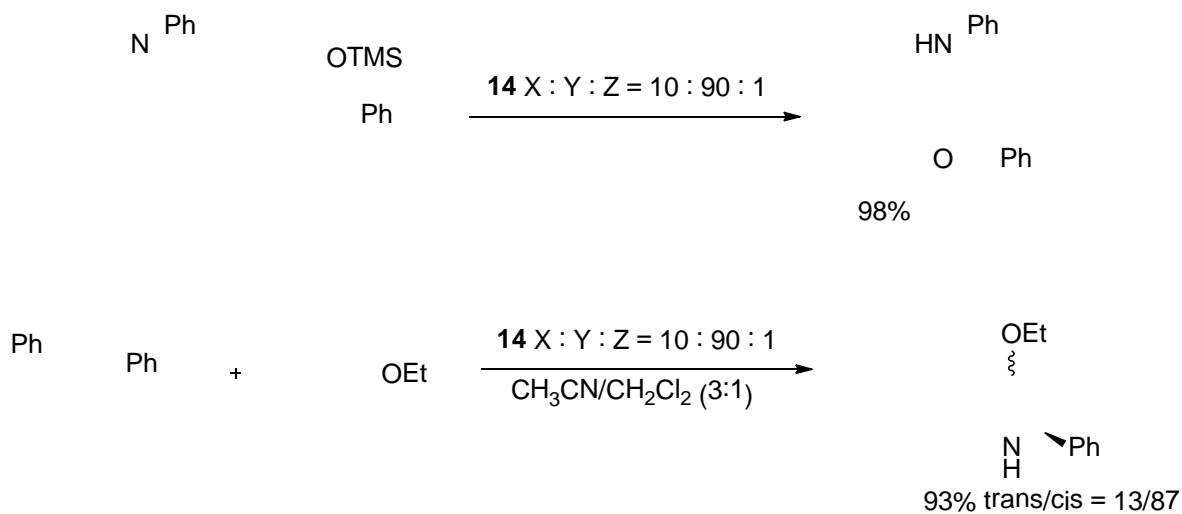
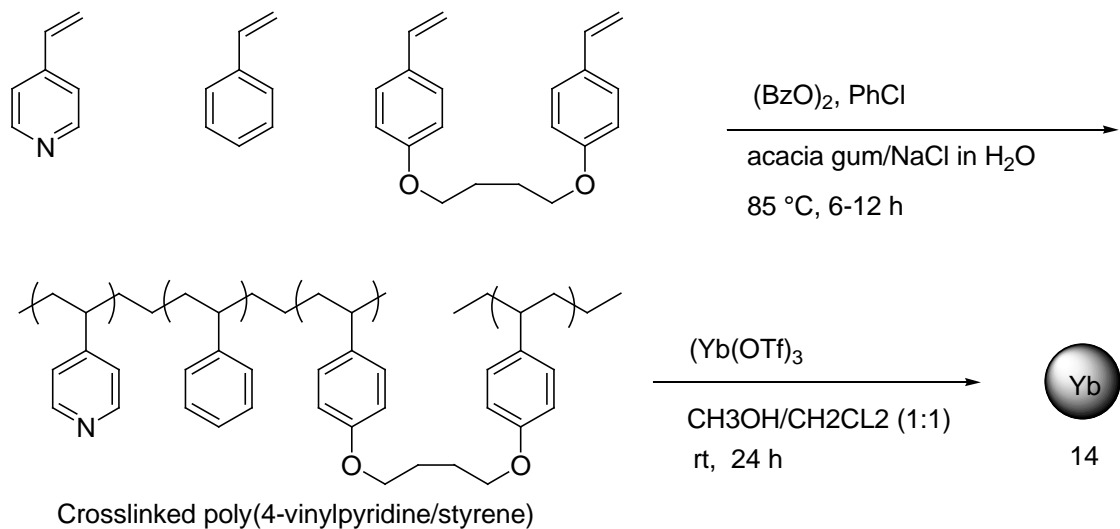
Scheme 10

Modified poly(ethylene glycol) (MeOPEG) supported chiral bisoxazoline ligand was synthesized for enantioselective carbon-carbon bond forming reactions such as Diels-Alder reaction, cyclopropanation and ene reaction in the presence of $\text{Cu}(\text{OTf})_2$ (Scheme 11).¹⁴



Scheme 12

Janda and coworkers developed a new method for the synthesis of cross-linked copolymer with $\text{Yb}(\text{OTf})_3$ (Scheme 12). The immobilized catalyst was tested for Mannich as well as Diels-Alder reaction.¹⁶



Scheme 13