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MAKING PLASTICS FROM CARBON DIOXIDE: CO-POLYMERIZATION OF EPOXIDES AND CO_2

Om Kumari, Ph. D.

Department of Chemistry, K K College Etawah (U.P.)

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Abstract

Since petroleum resources are predicted to be exhausted within the next century at the current rate of consumption due to global warming, there is a growing effort to develop new chemical processes using bio-renewable sources. Carbon dioxide is an abundant, inexpensive and nontoxic bio-renewable source. Immobilization by polymerization, reduction by metal catalyzed processes and chemical transformations are the processes by which CO_2 can be utilized. Apart from these processes, copolymerization of epoxies is very significant. Cyclohexene oxide, propylene oxide are the copolymers which form epoxies with CO_2 resulting the formation of cyclic carbonates as a major by product. Selection of copolymer are also important requires the component with least hindrance, C-O linkages and backbiting. Inoue group (aluminum catalysts) fulfills the basic requirements. Sometimes, salen metal complexes are also used in the formation of epoxies with CO_2. Formation of nano-particles by intermolecular cross linking and high activity Zn(II)-based catalyst can be used for asymmetric CHO-CO_2 copolymerization.

Keywords: *Co-polymerization ,reduction, chemical transformation, metal complexes.*

Introduction:

Global warming, is the term that denotes the gradual warming of the earth surface due to anthropogenic (human activity related) releases of green house gases (CO_2, CH_4, N_2O) due to industrial activity and deforestation resulting rise of sea level and change of climate, carbon dioxide is the major gas which is responsible for climatic change due to global warming. Since petroleum resources are predicted to be exhausted within the next century at the current rate of consumption, there is a growing effort to develop mew chemical process using bio renewable sources. CO_2 is an abundant in atmosphere, in expensive and non toxic bio renewable sources. Hence it might be an alternative raw material.

The amount of carbon dioxide in the air has been increasing during the recent years which may adversely affect the environment in the future CO_2 is the largest contributor to the green house effect. Moreover CO_2 is a very stable, linear molecule in which the oxygen atoms are weak lewis bases and the carbon is electrophile. Reactions of carbon dioxide are dominated by nucleophilic attacks at the carbon which result in bending of the O-C-O bond. Immobilization and utilization of CO_2 has become a challenge in the recent years. The most common reactions of CO_2 in this regard at pH range 7 in aqueous solution 25^0C and 1 atm pressure are as follows.

$CO_2 + e^- \rightarrow CO_2^-$ ($E^o = -2.14V$) (1)

$CO_2 + 2e^- + 2H^+ \rightarrow HCOOH$ ($E^o = -0.85V$) (2)

$CO_2 + 2e^- + 2H^+ \rightarrow CO + H_2O$ ($E^o = -0.76V$) (3)

$CO_2 + 4e^- + 4H^+ \rightarrow H_2CO + H_2O$ ($E^o = -0.72V$) (4)

$CO_2 + 6e^- + 6H^+ \rightarrow CH_3OH + H_2O$ ($E^o = -0.62V$) (5)

$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$ ($E^o = -0.48V$) (6)

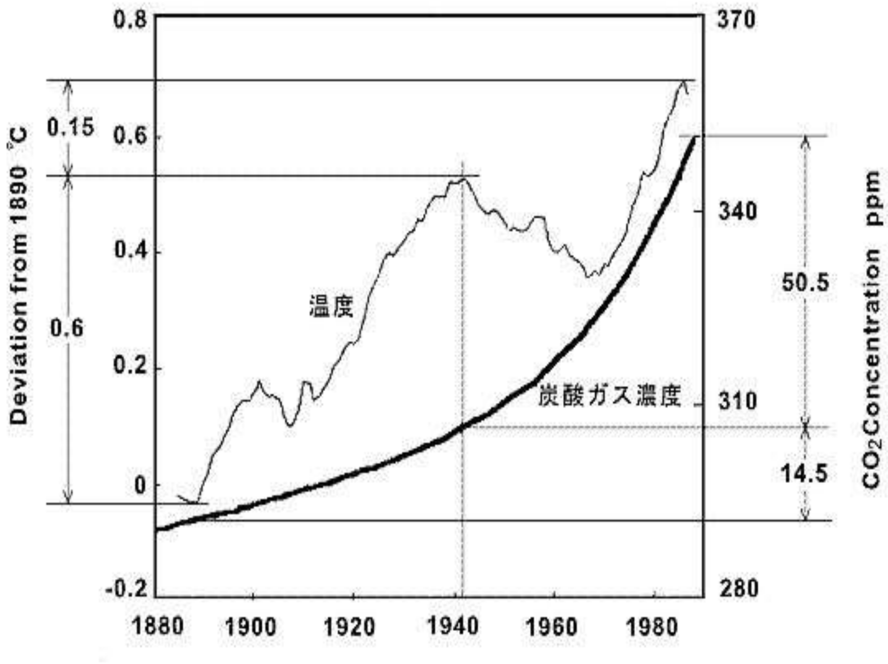


Fig1 the major reason of global warning

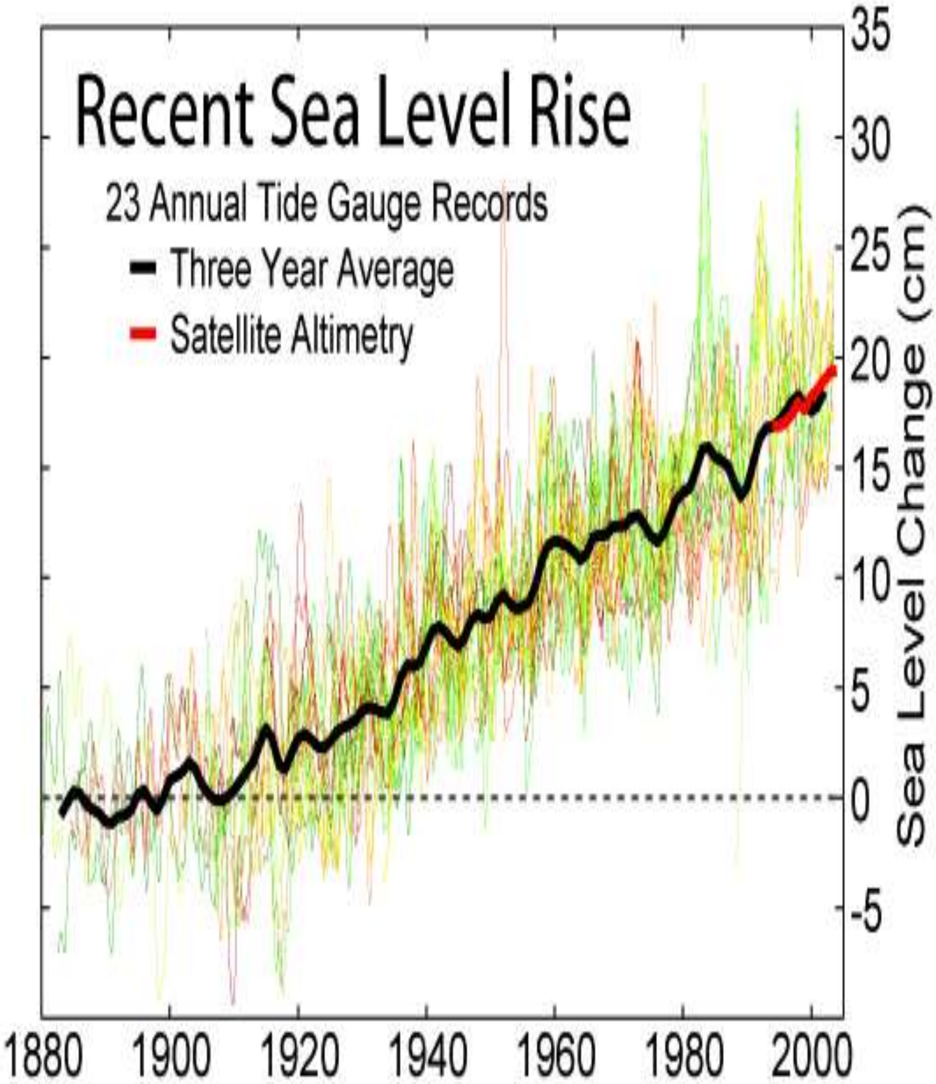


Fig2 Rising of Sea-level due to global warming

The main reaction compounds are formic acid, methanol, hydrocarbons and oxalic acid. This electro-reduction of CO_2 is of interest as a potential component of a carbond energy cycle i.e. CO_2 + energy→ methane → CO_2 + energy. The synthesis of CO_2 is a complex multi-step reaction with adsorbed intermediates, most notably adsorbed CO. the possible pathways to obtain chemicals from CO_2 and illustrated in figure3.

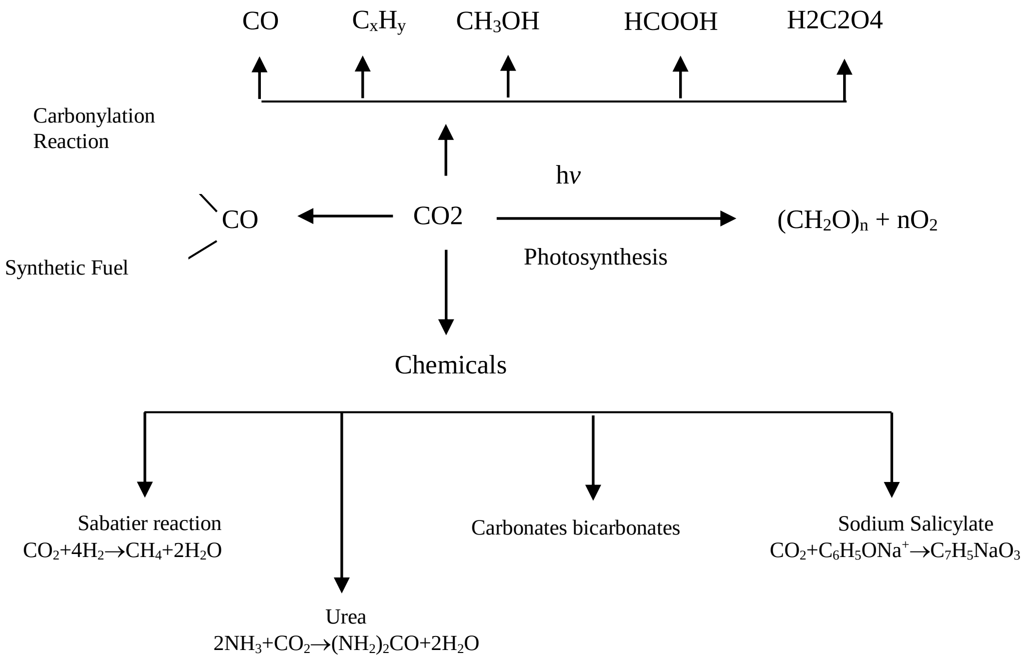


Fig3 Possible pathways to obtain chemicals from CO_2

Photosynthesis, photo catalytic and electro chemical reduction of CO_2 [1, 2] seems to be three of the most effective methods for the processing and recovery of the air carbond based sources. Different energies are needed to break a C-O bond in CO_2 and assist in converting it into useful products. The thermodynamic requirements for various CO_2 reduction reactions should be considered because of the stability and chemical inertness of CO_2 the necessary energy to carry our CO_2 recovery of the air carbon based sources can be generated by high temperatures, extremely reactive reagents, electricity or the energy from photon.

One of the most efficient way to immobilize CO_2 in polymerization of CO_2. Interest in the use of carbon dioxide as an industrial solvent has grown in recent years. The properties [3] of CO_2 (naturally occurring, renewable source that is safe to handle, no toxic and non-flammable) make it more environmentally friendly than many organic solvents that are commonly used in industry. The critical temperature and pressure of CO_2 (31.17^{0}C, 73.8 bar) are relatively low, making super critical CO_2 easy to obtain, another advantage for industrial application [4]. CO_2 can be used as a raw material for industrial processes as well as a solvent in oxidations, bio catalysis, hydrogenations and polymerizations [5]. The main limitation is the use of supercritical CO_2 in industry is its weak solvent power, in industry materials that exhibit solubility in supercritical CO_2 at moderate temperature and pressure ($T<100^0C$, P<200 bar) need to be synthesized.

The poly (propylene carbonate) polymers [6] can be synthesized from propylene oxide and carbon dioxide. The propylene oxide was dried with CaH_2 then isolated by distillation and kept under nitrogen. Reactions were conducted in a high pressure. The reactor was loaded with the catalyst, (0.05 mol %) and dried under vacuum. The initiator poly (propylene glycol) was dried under vacuum and then injected into the reactor. This was followed by the injection of dry propylene oxide. The reactor was then filled at room temperature with gaseous CO_2 to half the desired pressure. The reactor was filled the way after being heated to the reaction temperature. After running the reaction for 4to 5 hours, the reactor was depressurized and the polymer was dissolved in toluene. The polymer was isolated in a reparatory funnel. It was washed with an ammonium hydroxide/water mixture with saturated solution of NaCl.

Cooplymerization of epoxides and CO_2 can also be done by taking cyclohexene [7] oxide (CHO) and the formation of cycli carbonates as a major by product which is thermodynamically more stable than polycarbonates.

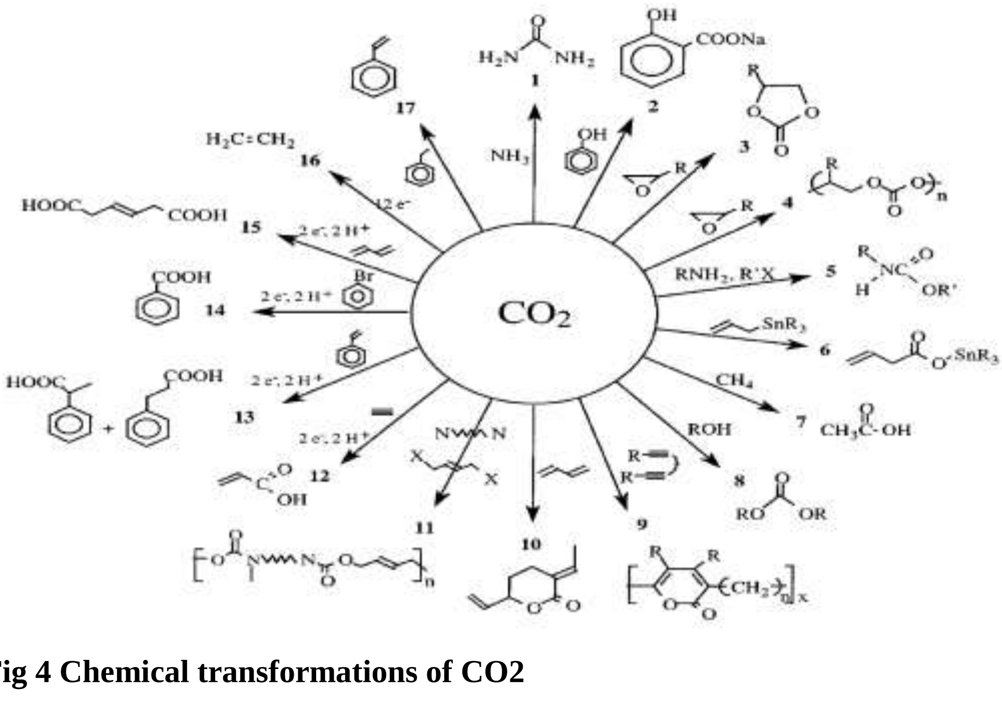
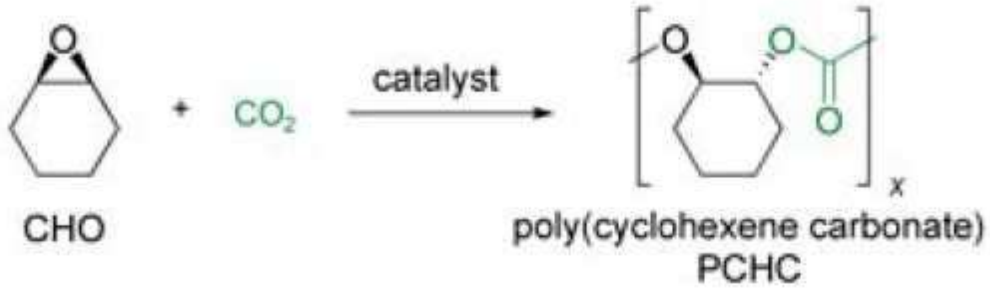
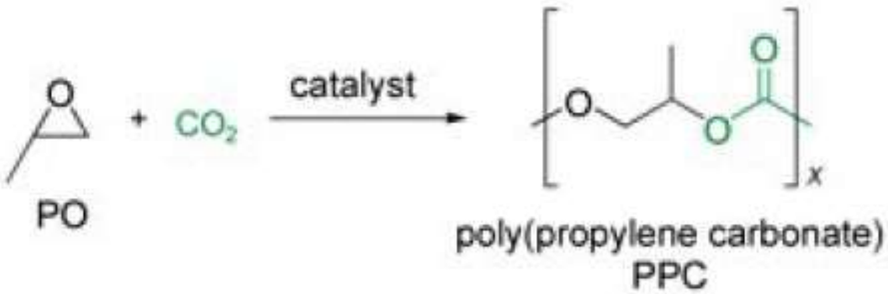


Fig 4 Chemical transformations of CO2



(CHO: cyclohexene oxide)



(PO: propylene oxide)

Fig.5 Copolymerization of epoxides and CO2

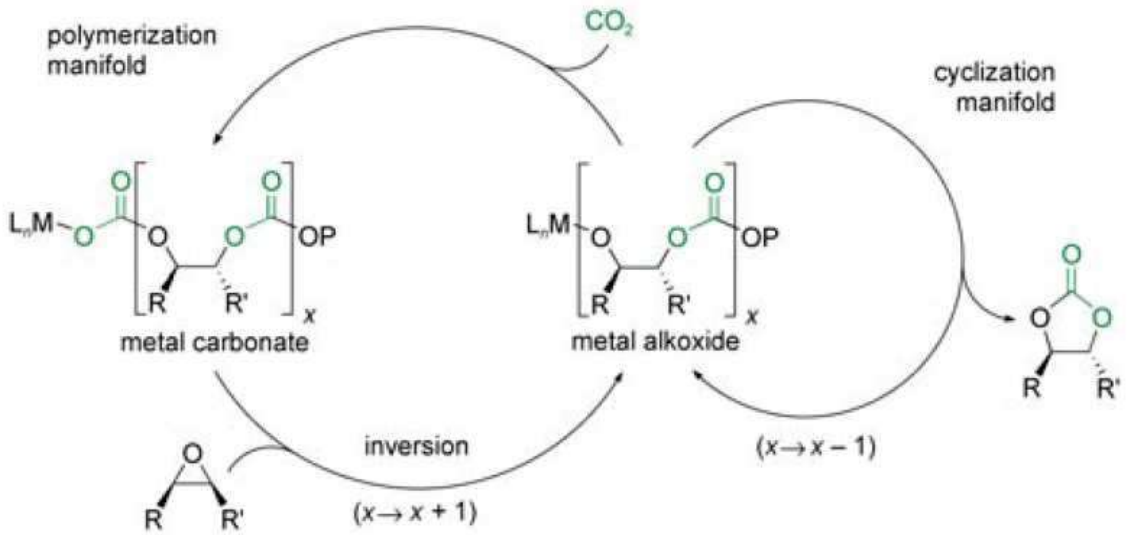
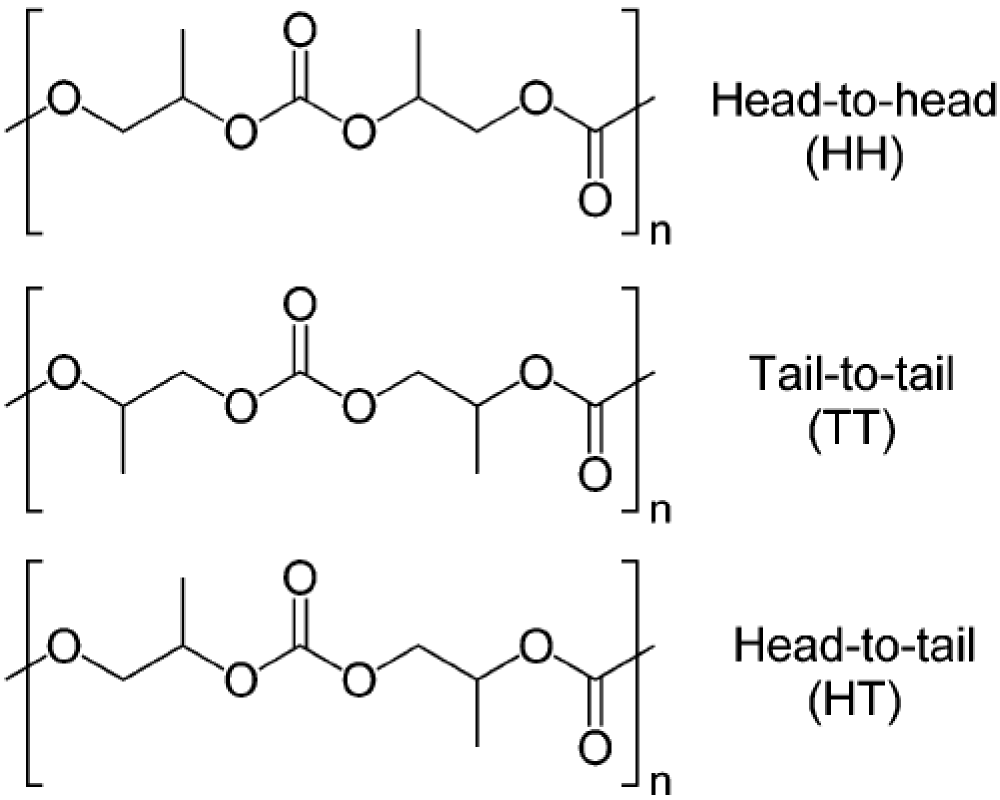
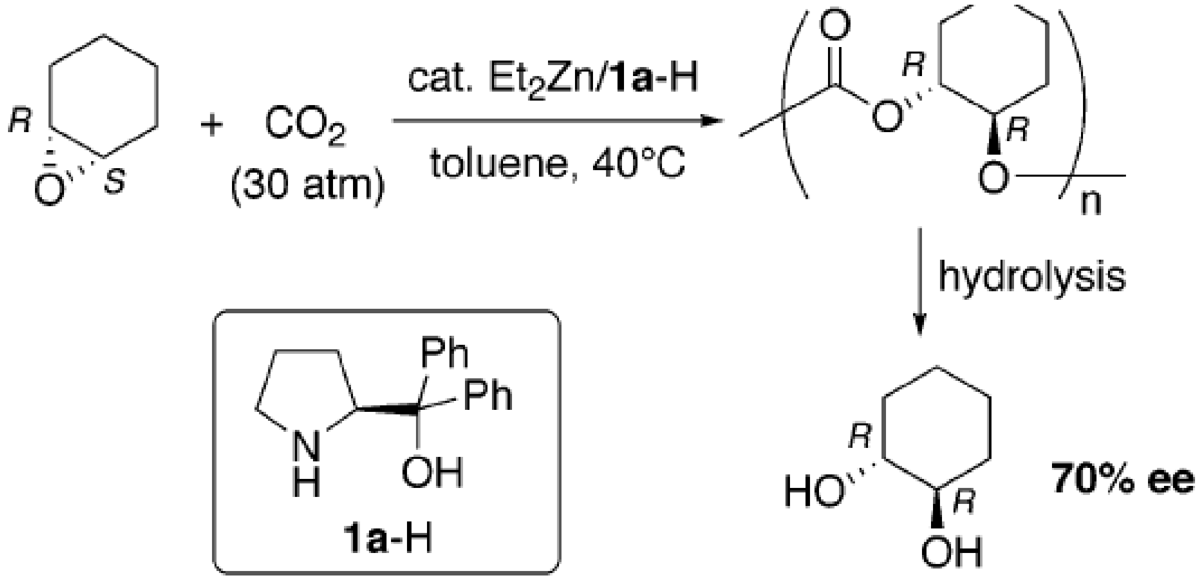


Fig.6 The basic mechanism of epoxides and CO2copolymerization and the formation of cyclic carbonates



Regiochemistry of PPC



Asymmetric Copolymerization of CHO and CO_2

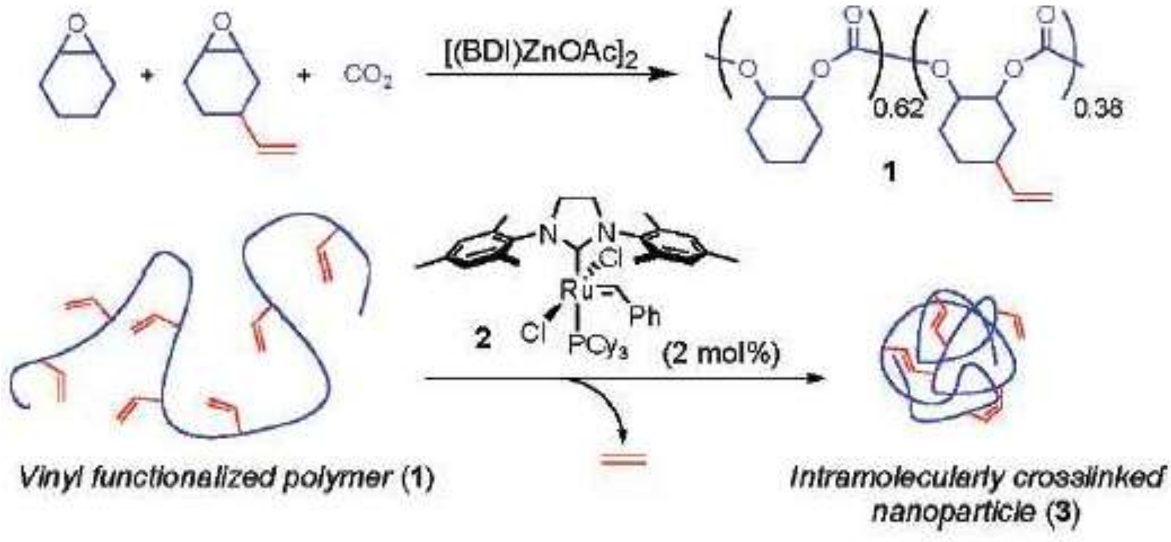


Fig.7 Synthesis of alkene crossing- linked polycarbonate nano-particles

Poly (propylene carbonate) is used as binder and to increase the toughness of epoxy resin. It is an unsuitable oxygen barrier therefore it can be used as a plastic material for the diffusion of oxygen. Getting rid of plastics is extremely difficult. Burning them can give off toxic chemicals such as dioxins, while collecting and recycling them responsibly is also difficult, because there are many different kinds and each has to be recycled by a different process. If we used only tiny amounts of plastics that would not be so bad, but we use them in astounding quantities. We are literally drowning in plastic we cannot get rid of. and we are making most of it from oil—a non-renewable that is becoming increasingly expensive. It's been estimated that 200,000 barrels of oil are used each day to make plastic pac. Broadly speaking, so-called "environmentally friendly" plastics fall into three types:

- **Bioplastics** made from natural materials such as corn starch
- **Biodegradable plastics** made from traditional petrochemicals, which are engineered to break down more quickly
- **Eco/recycled plastics**, which are simply plastics made from recycled plastic materials rather than raw petrochemicals.

The theory behind bio-plastics is simple: if we could make plastics from kinder chemicals to start with, they had break down more quickly and easily when we got rid of them. The most familiar bio-plastics are made from natural materials such as **corn starch** and sold under such names as EverCorn™and NatureWorks—with a distinct emphasis on environmental credentials. Some bioplastics look virtually indistinguishable from traditional petrochemical plastics. Polylactide acid (PLA**)** looks and behaves like polyethylene and polypropylene and is now widely used for food containers. According to NatureWorks, making PLA saves two thirds the energy you need to make traditional plastics. Unlike traditional plastics and biodegradable plastics, bioplastics [8-10] generally do not produce a net increase in carbon dioxide gas when they break down (because the plants that were used to make them absorbed the same amount of carbon dioxide to begin with). PLA, for example, produces almost 70 percent less greenhouse gases when it degrades in landfills. Another good thing about bio-plastics is that they are compost able: they decay into natural materials that blend harmlessly with soil. Some bio-plastics can break down in a matter of weeks. The cornstarch molecules they contain slowly absorb water and swell up; causing them to break apart into small fragments those bacteria can digest more readily. As the name suggests, these biodegradable plastics contain additives that cause them to decay more rapidly in the presence of light and oxygen (moisture and heat help too). Unlike bio-plastics, biodegradable plastics are made of normal (petrochemical) plastics and don't always break down into harmless substances: sometimes they leave behind a toxic residue and that makes them generally (but not always) unsuitable for composting. Anything that helps humankind solve the plastics problem has to be a good thing, right? Unfortunately, environmental issues are never quite so simple. Actions that seem to help the planet in obvious ways sometimes have major drawbacks and can do damage in other ways. It's important to see things in the round to understand whether "environmentally friendly" things are really doing more harm than good. When some biodegradable plastics decompose in landfills, they produce methane gas. This is a very powerful greenhouse gas that adds to the problem of global warming.

- Biodegradable plastics and bio-plastics don't always readily decompose. Some need relatively high temperatures and, in some conditions, can still take many years to break down. Even then, they may leave behind toxic residues.

- Bio-plastics are made from plants such as corn and maize, so land that could be used to grow food for the world is being used to "grow plastic" instead. By 2014, almost a quarter of US grain production is expected to be turned over to bio-fuels and bio-plastics production, potentially causing a significant rise in food prices.
- Some bio-plastics, such as PLA, are made from genetically modified corn. Most environments consider GM (genetic modification) crops to be inherently harmful to the environment.
- Bio-plastics and biodegradable plastics cannot be easily recycled. To most people, PLA looks very similar to PET (polyethylene terephthalate) but, if the two are mixed up in a recycling bin, the whole collection becomes impossible to recycle. There are fears that increasing use of PLA may undermine existing efforts to recycle plastics.

These days plastics are predominantly made from crude oil. In this context, renewable resources are becoming a more viable and promising alternative for the plastics industry. When plastics made from petroleum are burned, they release the carbon dioxide contained in the petroleum into the atmosphere, leading to global warming. The use of bio plastics offers significant advantages not only in an ecological sense but also in an economical sense. Bio plastics are a form of plastics derived from plant sources such as sweet potatoes, sugarcane, hemp oil, Soya bean oil and corn starch. Bio plastics are environmentally friendly because, compared with traditional plastics, their production results in the emission of less carbon dioxide, which is thought to cause global warming. They are also biodegradable, meaning that the material returns to its natural state when buried in the ground. Enzymes are used to break starch in the plants down into glucose, which is fermented and made into lactic acid. This lactic acid is polymerized and converted into a plastic called polylactic acid, which can be used in the manufacture of products after being heated and shaped. In addition, bio plastics are biodegradable. If something made of bio plastic is buried in the ground, micro-organisms will break it down into carbon dioxide and water. Bags made of bio plastic can be thrown away and buried with other biodegradable garbage, and there are a growing number of other uses for the materials as well, including artificial fibres, medical products, and construction materials. Poly(propylene carbonate)/starch (PPC/starch) composites with different starch contents were prepared by melt compounding. The biodegradability of the composites was studied by soil burial for a period of 6 months. FTIR study, thermal analysis and morphology observation indicated clearly the changes of the buried specimens. The weight loss curves and the molecular weight changes of the specimens revealed a three-stage biodegradation, corresponding to the propagation of microorganisms, the degradation of starch and the degradation of PPC. The experimental results showed that the addition of starch accelerated the degradation of PPC. Specimens with higher starch content exhibited greater weight loss in the second stage and smaller weight loss in the third stage.

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