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Perspective

Polymers from Renewable Resources: A Perspective for a Special Issue of Polymer Reviews

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The field of polymers derived from non-petrochemical feedstocks is gaining a great deal of momentum from both a commercial and academic sense. Using annually renewable feedstocks, such as biomass, for the production of new plastics can have both economic and environmental benefits. Fundamental research in the production, modification, property enhancement, and new applications of these materials is an important undertaking. The new materials, concepts, and utilizations that result from these efforts will shape the future of polymers from renewable resources. This issue of Polymer Reviews focuses on the production and properties of renewable resource polymers and highlights current trends and research directions.

Keywords renewable resources, polyesters, polycarbonates, vegetable oils, bio-derived polymers

1 Introduction

Polyethylene, polypropylene, polystyrene, polyethylene terephthalate, and polyvinyl chloride are all derived from petrochemical feedstocks. The utilization of fossil fuels in the manufacture of plastics accounts for about 7% of worldwide oil and gas.¹ These resources will arguably be depleted within the next one hundred years, and the peak in global oil production as estimated by some will occur within the next few decades.² At the time of writing, oil prices have reached an all time high and are generally subject to various socio-political influences. While the use of oil reserves and other related reserves for transportation and heating are certainly serious concerns, the chemical industry will also be faced with real issues associated with the use of an essentially non-renewable feedstock for the majority of their products.

We believe there is an urgent need to develop new synthetic routes to polymeric materials using renewable resources. In this review particular attention is paid to

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biomass, i.e., plant derived resources. Here, we highlight the potential for use of carbohydrate and triglyceride resources, derived from corn/sugar beet and oil seed producing plants respectively, to make plastics. Currently, there are only few commercial examples of plant derived plastics, mostly due to their relatively high cost vs. their petrochemical analogues. One future development which is expected to increase production and reduce costs of such renewable resource plastics is the biorefinery.³ The biorefinery is an integrated processing facility, analogous to the petrochemical refinery, producing fuel and chemical product streams from plants. It is expected to reduce costs by enabling cheaper biomass feed streams to be used, e.g., lignocellulosic biomass, and by more efficient use of all parts of the plant, e.g., by co-producing fuels and chemicals.

These renewable resource polymers are attractive from a feedstock point of view but also have benefits from a waste disposal perspective. Currently, the disposal of petrochemically-derived plastics is a major concern, especially in high population density countries like the UK, as the majority ends up in landfills where they are bulky and pervasive. Therefore, there is considerable legislative drive and consumer pressure for the development of biodegradable and/or recyclable plastics. In fact, many of the products that can be derived from renewable resources can also be rendered biodegradable under the appropriate conditions. Related to this behavior is the degradation of these polymers under biological conditions that are relevant to biomedicine applications. Many of the polymers that could be produced as commodity materials for day-to-day applications have had a history in the biomedical community because of their *in vivo* degradation characteristics. Thus the development of polymers from renewable resources is driven on several fronts.

In this special issue of *Polymer Reviews*, we present six articles that review distinct but interrelated areas of research in the renewable resource polymer arena. The first three contributions focus on the most promising renewable resource polymer today, polylactide. Polylactide is derived from plant-derived carbohydrates. The next two reviews emphasize the use of vegetable oils as renewable feedstocks, and the issue ends with a contribution on the copolymerization of carbon dioxide. While carbon dioxide is not plant-derived, the utilization of this molecule for the production of polymers could be critically important given its widespread abundance. Below we highlight these three areas and point out important research directions.

2 Polylactide

Poly(lactide) (PLA) has attracted significant attention as it is produced from plant derived resources, it also has suitable properties as a replacement material for polyolefins (e.g., in packaging) yet degrades to metabolites. It has recently experienced a renaissance due to its production by a number of companies.⁴ To make PLA, corn or sugar feedstocks are processed to yield D-glucose that is then fermented to yield lactic acid. The lactic acid is converted thermally and catalytically into its cyclic dimer, lactide. Using a suitably reactive catalyst, lactide will undergo ring-opening polymerization to yield PLA. The resultant plastic has properties related to polyolefins and polystyrene and can be converted into various products mainly in packaging and fiber applications.⁵ After use, the polymer can be degraded via hydrolysis to lactic acid and then metabolized to carbon dioxide and water. This can be quite a facile process under standard industrial composting conditions but it is worth noting that degradation is very slow at lower temperatures.

While PLA has been successfully utilized in a variety of applications that have been traditionally occupied by petroleum based polymers, implementation of PLA and

PLA-related materials on a broader scale has been somewhat thwarted. Two property issues that have limited PLA to some extent are its relatively low glass transition temperature and low impact strength. Furthermore, the commercially utilized catalysts/initiators for production of PLA, while useful, are not that highly evolved; new catalysts for the polymerization of lactide and other cyclic esters could significantly enhance the level of control over the polymerization process.

Addressing this latter issue, Platel et al. review progress in the synthesis of biocompatible (i.e., non-toxic) initiators for lactide polymerization. The key initiator parameters are the polymerization rate, molecular weight control, and stereocontrol. Further desirable features are a low cost, tolerance, abundance, lack of color or odor in the final product, and low toxicity. There has been much effort over the past decade on the development of new catalysts for the controlled polymerization of lactide and other cyclic esters, and several key reviews have appeared.^{6,7} There are myriad studies centered in the use of inorganic complexes in the ring-opening polymerization of cyclic esters. These complexes generally act via a so-called coordination-insertion mechanism where the catalyst activates the monomer for attack by an alkoxide ligand within the same complex. This is why the term catalyst and initiator are often used interchangeably in the community. Efforts to understand this mechanism in detail have been undertaken and several reports of very active catalysts have appeared. For example, β -diketiminate metal alkoxide complexes (M = Mg, Zn and Ca),⁸⁻¹⁰ phenoxy diamine zinc ethoxides¹¹ and homoleptic yttrium phenoxides¹² are all able to polymerize lactide at very high rates (Fig. 1).

In addition to achieving high rates of polymerization, stereochemical control in the polymerization of either racemic mixtures of *S,S*- and *R,R*-lactide or *R,S*-lactide have also been possible, enabling production of PLA with controlled tacticity. Since tacticity ultimately influences for example, crystallinity, melting temperature, and degradation rate these systems have proven to be quite useful in controlling the properties of PLA. For example, chiral salen Al complexes (Fig. 2) showed excellent selectivity for racemic lactide polymerization with the rate constant for the addition of the *R,R* enantiomer being 20 times greater than that for the *S,S* enantiomer. As a result, these initiators yielded "stereo-block" PLA from racemic lactide. In addition, syndiotactic PLA could be produced using the same systems and *R,S*-lactide.^{13,14} Other selective catalysts have been explored, and this has been a fruitful area of research.^{15,16}

Recent efforts in this area have included the decoupling of the catalyst and the initiator in "activated monomer" polymerizations. In these systems the catalyst coordinates and activates the cyclic ester and attack of an exogenous nucleophile (typically an alcohol) is the key propagation step. In recent manifestations of this type of polymerization a

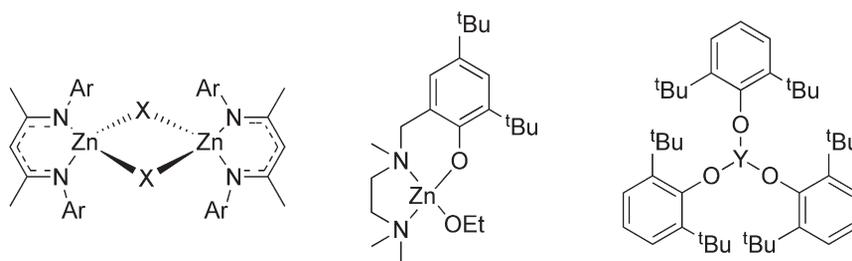


Figure 1. Structures of representative initiators/catalysts exhibiting very rapid lactide polymerization rates. Ar = 2,6-*i*Pr₂C₆H₃ or 2,6-Pr₂C₆H₃ or 2,6-Et₂C₆H₃, X = OiPr.

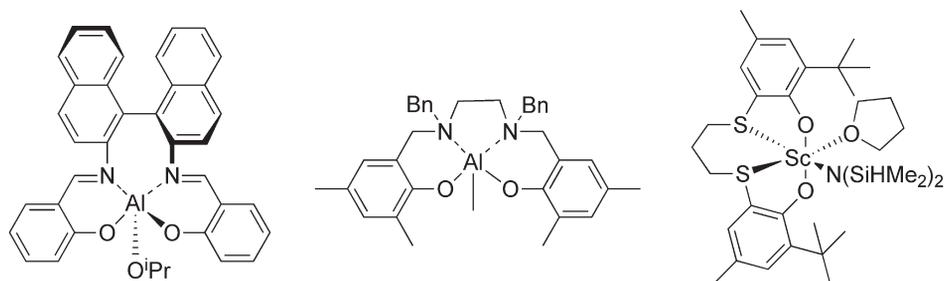


Figure 2. Representative structures of initiators/catalysts for the stereocontrolled polymerization of lactide.

variety of organocatalysts have been developed that give excellent polymerization control, good rates, and versatile endgroup incorporation.^{7,17}

The PLA materials produced by these catalytic methods are generally either atactic or isotactic. The atactic variants are completely amorphous and have a glass transition temperature around 55°C. Isotactic PLA has a similar glass transition temperature, but is typically semi-crystalline with a melting point around 170°C. While the thermal properties of these different materials are distinct, the proximity of the glass transition temperature to room temperature and/or service temperatures renders PLA unsuitable for various applications that require structural integrity at higher temperatures. Therefore, there have been several efforts aimed at increasing the glass transition temperature of PLA or lactide-derived materials. This is the topic of the contribution by Baker et al. The typical approach involves the synthesis and polymerization of lactide-related cyclic esters. These monomers often carry bulky or rigid side chains that can, in principle, limit segmental motion thus increasing the glass transition temperature. The research work in this area has been somewhat limited, but there has been recent activity given the importance and realization that somewhat modest increases in the glass transition temperature of polylactide-based materials could significantly widen its application base.

Lowering of the glass transition temperature in PLA has also been explored, but this has typically been done in an effort to toughen PLA. In the contribution by Anderson et al., this research area and other PLA toughening approaches are reviewed. Toughening agents for PLA have generally aimed at improving either the impact strength of the material or the tensile toughness. However, improvements in either often come at the expense of reductions in modulus and/or tensile strength. In fact, it can be difficult to make comparisons between studies because the entire property profile for a given toughening approach is often not presented. In addition to lowering the glass transition through plasticization, many rubber-toughening approaches have been explored. In the latter approach there have been various materials blended with PLA. In addition to binary blends, several ternary blends that include a suitable compatibilizer have been explored.¹⁸

One of the key concerns in any blending strategy with PLA is the original and environmental compatibility of the blend partner. Many materials have been blended with PLAs, however, only a subset have renewable origins and/or are biodegradable. Recent efforts in the PLA toughening area have focused on the inclusion of renewable materials in PLA composites. In many cases the toughening agents are also polyesters and therefore blending conditions have to be carefully controlled so that the degradation

and the transesterification processes can be properly managed.¹⁹ This highlights one of the central challenges in the utilization of renewable polymers: renewable polymers are generally more thermally, chemically, hydrolytically, and oxidatively sensitive as compared to petrochemical-derived materials.

3 Vegetable Oil-Derived Polymers

Vegetable oils, such as soybean oil, palm oil, and rapeseed oil, are extracted primarily from the seeds of oilseed plants and have a wide variety of applications: as foods, fuels (biofuels), lubricants, paints, cosmetics, pharmaceuticals, plasticizers, and construction materials. They are also attractive monomers for polymer chemistry due to their natural abundance and reactive functionality. However, their use as monomers presents challenges due to their heterogeneous and variable structures. Indeed, it can be expensive to separate and extract the different triglycerides present because the oils are typically expressed in low concentrations and the composition of a particular oil can vary seasonally. Recent advances in genetic engineering have heralded breakthroughs: for example the oleic acid component of variant sunflower oil can be increased to over 92%.²⁰ The key chemical building blocks of vegetable oils are triglycerides: triesters of glycerin and fatty acids (Fig. 3). Of the five commonly occurring fatty acids, two are saturated (palmitic and stearic) and three are unsaturated (oleic, linoleic, and linolenic).

Triglycerides monomers are of interest due to their olefinic functionalities which could yield a cross-linked polymer directly.²¹ Direct polymerization of oils has been used to make ink resins, but these do have to be post-cured after application by oxidative coupling. Some other vegetable oils, like tung and linseed oil, are either cross-linked

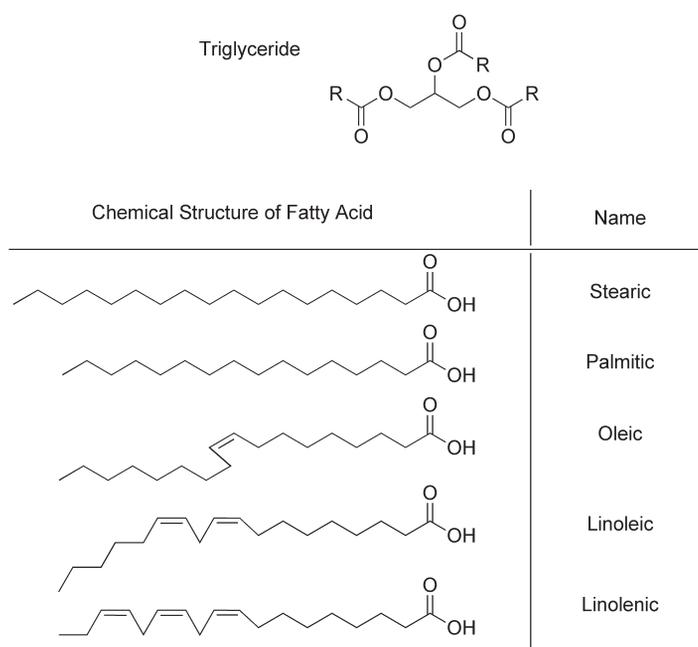


Figure 3. The structure of triglycerides and the five most common fatty acid substituents.

directly, or with other additives, in varnishes, paints, and floor coverings (linoleum). However, to make well-defined monomers and polymers the triglyceride oils need to be separated and functionalized. Functionalization is frequently achieved by reactions at the olefin functional groups for unsaturated fatty acids. Commonly used olefin functionalization reactions include epoxidation, isomerization,²² hydroformylation, reduction, and metathesis reactions. In this issue Petrovic et al. review the preparation of polyurethanes from triglyceride derived polyols. The polyurethanes are prepared by the reaction between a vegetable oil derived polyol and various isocyanates. Petrovic's research has focused on the preparation of polyols by the direct oxidation of oils, by epoxidation of the olefin functional groups followed by ring opening,²³ by hydroformylation,²⁴ ozonolysis,²⁵ and transesterification. The polyols are subsequently used to prepare polyurethanes whose structures depend on the type of triglyceride used, the nature of the isocyanate group and the degree of cross-linking. These polyurethane materials are characterized with particular attention being paid to their degradability and biocompatibility.

Industrially, it is often useful to hydrolyze the triglycerides to produce glycerol and fatty acids, indeed this process is used in biodiesel manufacture. Following hydrolysis, the water and lower boiling fractions are removed by distillation and then a series of vacuum distillations enables separation of the fatty acid components. Jain et al. review the incorporation of fatty acids into polyesters and polyanhydrides. Their focus is on the biocompatibility of fatty acid derived polymers and on producing polymers for medical applications. For biomedical applications, fatty acids are attractive as they are naturally occurring and processable in the body and are hydrophobic, thus retaining an encapsulated drug for longer periods of time.²⁶ The incorporation of fatty acids into polyesters or polyanhydrides is somewhat problematic because most naturally occurring fatty acids only have one carboxylic acid group and therefore can only be used as chain end groups. However, this limitation can be overcome by using naturally occurring bifunctional fatty acids such as ricinoleic acid or bile acid or by chemical functionalization of fatty acids (e.g., by dimerization through their double bonds). Jain et al. focus their review on the incorporation of ricinoleic acid which is a naturally occurring C₁₈ acid, produced from the hydrolysis of castor oil, with a

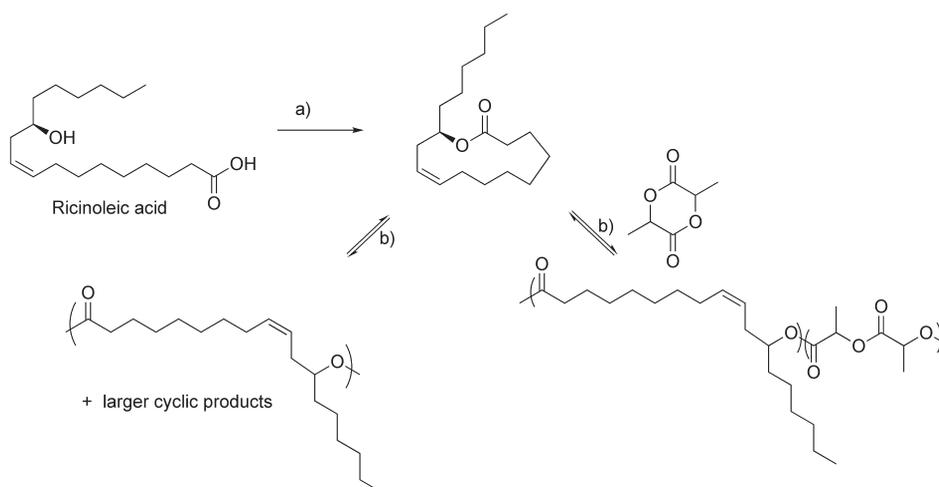


Figure 4. Preparation of polyesters from ricinoleic lactone. Conditions: a) N,N'-dicyclohexylcarbodiimide, dimethylaminopyridine, HCl, CHCl₃, b) Sn(Octanoate)₂, 135°C, 24 h.

cis-configuration double bond at C₉ and a hydroxyl functionality at C₁₂ (Fig. 4). It has been incorporated into polyesters by condensation polymerization with anhydride end capped poly(sebacic acid).²⁷ Recently, it has been found that ricinoleic acid can be cyclized to produce a series of lactones which can be oligomerized or copolymerized by standard ring opening polymerization techniques (Fig. 4), including using the catalysts such as those described in the review by Platel et al. These copolymers of ricinoleic acid are biodegradable, undergoing degradation in a couple of weeks under *in vitro* physiological conditions. The polymers are also suitable for drug delivery applications as they release model drug candidates (*cis*-platin) as they degrade.

4 Carbon Dioxide as a Feedstock

Carbon dioxide is an interesting synthetic feedstock since it is abundant, inexpensive, non-flammable, and a waste product of many chemical processes. Although it is estimated that nature uses CO₂ to make over 200 billion tons of glucose by photosynthesis each year, synthetic chemists have had little success in developing efficient catalytic processes that exploit this attractive raw material. The activation and application of carbon dioxide as a C₁ source are rather limited, for example in the organic synthesis arena only urea, salicylic acid, and some cyclic carbonates can be viably produced from CO₂. However, carbon dioxide can be copolymerized with heterocycles (epoxides, aziridines, episulfides) to yield a range of novel alternating copolymers. Of these, polycarbonates represent a very promising class of materials; they are thermoplastic materials and can be produced in reasonable efficiency from CO₂ and epoxides. Initial studies have indicated that aliphatic polycarbonates can be recycled via hydrolysis reactions and in some cases biodegraded.

In 1969, Inoue reported the zinc catalyzed sequential copolymerization of carbon dioxide and epoxides as a new route to polycarbonates.²⁸ This landmark discovery uncovered, for the first time, the potential to use carbon dioxide as a feedstock for large scale polycarbonate synthesis. In the proposed copolymerization cycle (Fig. 5) a Lewis acidic metal species binds and ring opens an epoxide, generating a metal alkoxide species. Carbon dioxide inserts into the metal alkoxide bond giving a metal carbonate and this species can bind and ring open a further molecule of epoxide; repetition of the cycle ultimately leads to the production of high molecular weight polymer.²⁹ A variety of homogeneous and heterogeneous Lewis acidic metal complexes initiate the polymerization, including Zn(II), Co(II), and Cr(III) alkoxides, carboxylates, and carbonates.³⁰ However, the structures of the catalytically active species are difficult to determine due

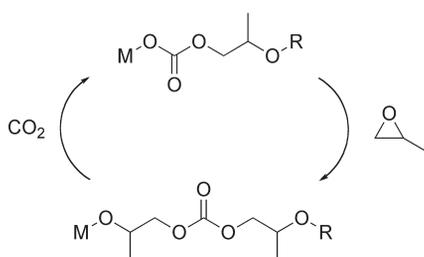


Figure 5. Copolymerization of carbon dioxide and propylene oxide to yield poly(propylene carbonate). M = metal center (e.g., Zn(II), Co(II), Cr(III)), R = growing polymer chain.

to the tendency for such metal initiators to aggregate. Therefore, a significant factor precluding the commercial preparation of polycarbonates using this method is their low catalytic activity, for example a typical homogeneous polycarbonate catalyst produces 500 g of polymer per g of catalyst. When compared to those applied in olefin polymerization (where 1 g of catalyst will typically give 10^6 g of polymer) it is clear that there is much scope for improvement.

Luinstra reviews developments in the alternating copolymerization of carbon dioxide and propylene oxide to yield polypropylene carbonate (PPC). Although PPC has been known for nearly 40 years it has yet to be commercialized. There have been several developments in the use of heterogeneous zinc catalysts and in particular zinc glutarate to make it.^{31,32} Although the detailed mechanism of these species is still not fully understood, it is now known that the following features are desirable:

- i. covalently unsaturated zinc sites on the surface of the catalyst and
- ii. a crystal structure related to that formed by zinc glutarate.³³

The properties of polypropylene carbonate are also examined, in particular its thermal degradation which occurs via a chain end scission mechanism at 200°C. The low thermal degradation temperature is problematic for processing by common thermoplastic techniques such as molding, mixing or extrusion. The use of co-monomers and end-groups has improved the thermal stability.³⁴ Luinstra outlines how the properties of PPC depend both on the synthesis, catalysts and on any co-monomers used. The biodegradation properties of the polymer are also reviewed.

5 Conclusions

Polymers from renewable resources are here to stay. There is no question that these materials will play an ever increasing role in the commodity plastics marketplace as well as continue to be important in niche medical markets. This will likely not only stem from economic and environmental benefits, but also from the new property profiles that renewable resource polymers can exhibit, such as biocompatibility and biodegradability. Fundamental research efforts in this field are set to continue and are really just beginning. It will be very important to uncover the detailed structure-property relationships for these novel plastics and in particular to develop efficient methods to predict their degradation properties. Another hurdle is that the modern polymer industry has been based almost exclusively on materials from petrochemical feedstocks. The new renewable starting materials are not the traditional olefinic materials but are highly oxygenated carbohydrates. Carbohydrate chemistry has focused for the last hundred years on developing intricate protection-deprotection strategies for use in pharmaceuticals/medicine. Plastic applications will require the discovery and development of carbohydrate transformations involving few steps and in high yield. A promising area for future development will be catalytic chemistries such as carbohydrate dehydration or carboxylation. There are also many challenges in handling and converting these new feedstocks and in controlling the resultant polymer properties in economically and environmentally sound ways. In the short term, improvements and developments of reactions such as esterification, etherification, and redox reactions of carbohydrates would enable the incorporation of renewable feedstocks into plastics. In the longer term, the use of lignocellulosic feedstocks or mixed waste biomass streams are important targets as they will significantly reduce the cost. We are optimistic about the future of polymers from renewable

resources. Many important advances have been made (especially over the past decade) and more are yet to come. While renewable polymers are not poised to take over polyethylene or polypropylene any time soon, their penetration into both everyday and specialty products will be more evident in the future.

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