Polymers from Renewable Resources

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Abstract

In the modern world, the importance and use of macromolecular materials based on renewable resources declined owing to the rise of the fossil fuel-based resources from which a large number of lower-cost polymers could be synthesized. These polymers had unique, in general, superior properties than the polymers obtained from renewable resources. The high price of renewable resources limited polymers from renewable resources in their use. However, changing world economics have again stressed the importance of renewable resources in the advancement of research and applications. Recent years have witnessed a paradigm shift since dwindling reserves of fossil fuels, including resources supporting the environment and increasing price of fossil fuels. Recent advances in the synthesis and properties of polymers from renewable resources with novel properties and potentially lower costs have boosted the hopes that the replacement of the conventional fossil-based polymers with these renewable polymers will be permanent and economically feasible.

Keywords: Biodegradable renewable materials, bioplasticizers, starch, cellulose, plant oils, polyhydroxyalkanoates, nanocomposites, elastomers, thermoplastics.

1.1. Introduction

Macromolecular materials based on renewable resources have found applications in various human activities for centuries. In the modern world, their importance and use declined owing to the rise of the fossil fuel-based raw resources from which a large
A number of low cost polymers could be synthesized. These polymers had been, in general, inferior properties than the polymers obtained from renewable resources. The high price of renewable resources based polymers also caused the substitution in their use. However, changing societal economical have caused reductions in the use of renewable materials for many resources to the detriment of research and development. Resources for such a paradigm shift were declining: amounts of fossil fuels, increasing awareness regarding the environment and increasing price of fossil fuels. Apart from that, recent advancements in the synthesis and properties of polymers from non-renewable resources with general properties and potentially lower costs have hindered the hopes of the replacement of the conventional fossil based polymers with these materials. A lot of research effort has been ongoing in order to further explore the novel renewable resources as well as to modify the currently existing polymers derived from renewable polymers. In a recent comprehensive review on the subject [11], Contandri also emphasized the importance associated with these materials and also provided readers numerous estimates to be done in order to realize the true commercialization of such materials. These are many polymers which are more abundant in nature than and have also received maximum research attention like cellulose, chitin, starch etc. These materials find use either in the natural-based fields or offer suitable building or surface modifications. The hydroxyl groups in polysaccharides are commonly used to modify these materials and to add required chemical functionality. As the C-H groups are involved in the modification in reactions, the corresponding grafting processes include the typical condensation reactions like esterification, etherification, and formation of very important esters etc. Figure 1.1 shows the basic structures of one of the most abundant polymer which is cellulose. Cellulose, chitin, starch etc. The factors of applications of these polymers have also diversified: these polymers are used not only as materials, but also as fibers or fibers for reinforcement of other polymers. Apart from this, research on renewable most abundant polymers, many other interesting polymers with good properties have also been developed in the recent years, which makes the applications spectrum of these materials very wide. Examples of a few of polymer materials derived from renewable resources are discussed in the next sections.
Figure 2.1. Structure of the most abundant polysaccharides in nature: (I) cellulose, (II) chitin, (III) chitosan, (IV) amylose, and (V) amylopectin. Reproduced from reference 1 with permission from American Chemical Society.
11.2. Naturally Renewable Methylenic Butyrolactones

Kim et al. [12] reported the polymerization of naturally renewable methylenic butyrolactones by half-sandwich isostructural metal carboxylate complexes, such as methylenic butyrolactone-derived (MBut) and p-methoxybenzyldiene-methylenic butyrolactone (MOMB) complexes containing a diethylidene isostructural ligand, were used for the coordination to molybdenum polyoxoanions and stable molybdenum butyrolactone complexes. The polymerization of these molybdenum butyrolactone complexes (Figure 1.2) shows the schematic of methylenic butyrolactone monomers (MButOMo), and their polymers (MButOMo), along with comparisons with MBut and MButAC. Structures of half-sandwich H2Co/MBut complexes are also shown. The authors observed several structural differences in catalytic behavior of half-sandwich H2Mo catalysts and molybdenum complexes, suggesting a new catalytic mechanism for the polymerization of methylenic butyrolactones. All three catalytic conditions exhibited comparable activity for polymerizations of MButOMo, with H2Mo catalysts exhibiting lower activity and monomer conversions for all monomer with a 0.2:1 molybdenum butyrolactone feed.

Milgrom et al. [13] similarly reported the limiting polymerization of naturally renewable methylenic butyrolactone complexes with molybdenum complexes.
1.3 Renewable Rosin Acid-Degradable
Caprolactam Block Copolymers

Williams et al. [4] reported the synthesis of block copolymers based on renewable rosin acid-degradable resins by atom transfer radical polymerization using expending polymerization. For the two-step sequential polymerization, either poly(2-sulfohexoxyethyl dimethacrylate) (SDEA) or poly(e-caprolactam) (PCL, Br) were used as initiators. Two-step sequential polymerization resulted in the generation of well-defined block copolymers with low polydispersity. One-step polymerization was also carried out with three different sequential feeds of ARFDA and a C1, initiator. The control of one-step polymerization was shown to depend on the interactions of competing ATRP catalysts and RAFT catalysts.

Figure 1.4 shows the TSC thermograms of the PCL, Br homopolymer and the block copolymers. PCL, Br exhibited a characteristic exothermic endothermic melting peak at approximately 220°C. The thermal behavior of diblock copolymers depended on the length and fraction of the PCL, block in the block copolymers. In the blocks...
1.4 Plant Oils as Platform Chemicals for Polymeric Synthesis

Vijgania et al. [61] reviewed the importance of plant oils as platform chemicals for the synthesis of polymeric materials. In one such example, synthesis of water-soluble chitosan/polysaccharide for polymeric-saccharide synthesis through reaction involving chitosan was demonstrated. As shown in Figure 1.6, functionalization of chitosan monomer oil with carboxylic polyethylene glycol was achieved via photoproduction and subsequent reduction. Chitosan monomer oil was used for polyvinyl alcohol with single oxygen generated
with a high-performance liquid chromatograph equipped with a photodiode array detector (HPLC-DAD) as an MS detector in an unoptimized chromatographic condition. By following this process, a mixture of isomeric allylic hydroxyamides were obtained as shown in Figure 1d. These were further reduced to
unesterified hydroxylated oil using sodium benzyldihydroxide as shown in Figure 1.6b. The authors transformed the resulting allylic alcohols into the saturated analogues as shown in Figure 1.6c by hydrogenation at room temperature using 5% charcoal-supported platinum as catalyst. The polyols were then used for the synthesis of polyurethane polyols. Similarly, synthesis of vegetable oil-based polyols through polycondensation of C=O double bonds & subsequent hydrolysis of ester groups and synthesis of fatty acid-based polyols etc. were reported.

1.5 Biocompatible Stereocompatible Polyols

Hesse et al. [6] reported the synthesis of biocompatible stereocompatible polyols from click chemistry step growth polycondensation of diol and diisocyanate dihydroxylates. Figure 1.7 demonstrates the schematic of synthesis of these polyols. These biocompatible polyols had a good thermal degradation resistance at temperatures to 10% degradation values observed to be in the range of 350°C ± 5°C.
Theaconites can be converted to high-molecular-weight polymers. The polymers displayed high glass transition temperatures in the range of 102-106°C. The molecular weights of the generated polymers were also high, and they led to the range of 2-10 kg/mol. The polymers showed good solubility in DMF and DMSO at room temperature. The authors reported that the molecular architecture (structure) of a crucial parameter controlling the generation of polymers with high glass transition temperatures. Several polyglycerols were synthesized to exhibit high volume of PDI (1.05-2.5) indicating homogeneity of molecular weight distribution. The authors have also provided some additional information on high molecular weight species due to the formation of aggregates in hot DMSO and at lower molecular weight species.

1.6 Polymers from Naturally Occurring Monocyclones

Kharazmi et al. [8] reported the controlled polymerization of cyclic diene prepared from the dicyclic closing methathesis of naturally occurring monocyclus as shown in Figure 1.8. The monocyclus monomers (1) were obtained from plants or from the pyrolysis of pentaerythrityl tetraacrylate and the cyclic diene 1-methylcyclohexene-2-one could be prepared from 1 by ring closing methathesis reaction. Polymerization of cyclic diene was studied using radical, anionic, and cationic polymerization. Radical polymerization of cyclic diene using radical initiator AIBN exhibited low conversions in hexane solution. However, polymerization led to a polymeric product in 58% yield after 20 h at 80°C. Anionic polymerization was carried out using sec-butyllithium (0.10 M) as initiator and polyethylene monomers were observed to be insoluble at low temperature. In the case of

Figure 1.8 Synthesis scheme for the preparation of polyethylene from naturally occurring monocyclus. Reproduced from reference [8] with permission from American Chemical Society.
Krasny et al. [18] reported that group transfer polymerization (GTP) of itaconic acid ester diol monomers in a methacrylate monomer, 2-(methacryloyloxy)ethyl diglylate (MAAG), the monomer most resistant to nucleophile substitution, was not suitable for preparing starch polyesters of methacrylate monomers with controlled molecular weight distributions. The MACI' monomers were synthesized by copolymerization with a hyperbranched methacrylate, a hyperbranched methacrylate, and a dimethacrylate in addition, respectively, on polyglycidyl, dimethylglycidyl, and other polymers and that diglylate ester. The authors found that the polymeric chain polymerization of the simplest ester of diglycidyl, methyl diglylate (MDG) using various conventional polymerization methods or group transfer polymerization (GTP), which is a method for the synthesis of starch polymers, with the methacrylate monomers could not be polymerized, those, requiring the introduction of a methacrylate monomer.

Figure 1. The demonstration of the synthetic strategy followed for the precipitation of MACI' and its homologues and copolymerizations with conventional methacrylates. Elongation polymers of MACI' contained a range of methacrylate weight values and relatively narrower distributions, corresponding to KU-50 lower than IIo for all cases. Various copolymerization vectors synthesized using GTP for copolymerizable MACI' with methacrylate carboxylates (OMAA, 2,2-dimethyl-2,4pentene-1,5-diol monoester chloride (DMMAC), or ethylene glycol dimethacrylate (EGDMA)), which CEP tracer of which were shown in Figure 1.5a. 
1.8 Oxypropylation of Rapeseed Cake Residue

Seo et al. [19] studied the oxypropylation of rapeseed cake residue generated in the biodiesel production process. The authors carried out the reaction by suspending the rapeseed cake residue in propylene oxide in the presence of a basic catalyst and heating the resulting mixture at 110°C in a nitrogen atmosphere which led to the synthesis of the propylene oxide oligomers with good characteristics. Almost total conversion of the solid substrate into pelal was achieved. Figure 1.10 shows the
Sample weight (%) vs Temperature (°C) of Sampled pellets and epoxypropylated product.

Figure 1.49: TGA thermograms of the sampled pellets and epoxypropylated product. Significant differences in the thermal behavior become apparent in the epoxypropylation reaction were observed. The hydrosoluble character of the sample decreased after epoxypropylation, as the extent of the first mass loss, from room temperature to about 150°C, associated with the evaporation of water present in the samples, decreased. The introduction of propylene oxide (PO) also led to a decrease in the degradation temperature of the epoxypropylated product. The differential scanning calorimetry (DSC) analysis revealed that the epoxypropylated product was a branched polymer bearing numerous C=O groups per macromolecule with a glass transition temperature of 35°C.

1.9 Copolymerization of Naturality Oxidizing Lignin Monomer

Sarkar et al. [10] reported the living radical chain copolymerization of naturally occurring lignin monomers with maleimide. Figure 1.50 shows the schematic of the reaction between lignin (LH) and phenylenediamine (PA). LH, a radical, transfers HS_2, while MA, a radical, exclusively reacted with HS_2, thus leading to 1:2 radical copolymerization.
The copolymerization reactions were examined in THF/6% amyl alcohol and 6% dimethylethylendiamine (AAMN) as a radical initiator at 60°C. The glass transition temperatures obtained for the copolymers were significantly higher (220–250°C) owing to the higher incorporation of maleimides as well as the rigid allenic structure of the sequence. Apart from that, controlled/living radical polymerization was carried out with a reversible addition fragmentation chain transfer (RAFT) agent, which led to the synthesis of end-to-end sequence-regulated copolymers with controlled molecular weights.

1.1.0 Polymerization of Lactides

Dusselier and co-workers [11] reported the ring-opening polymerization (ROP) of lactides catalysed by metalloaminocarboxylates. All the complexes used in the study were observed to be very effective catalysts for the ring-opening polymerisation of lactides at ambient temperature, producing polymers with controlled and narrow molecular weight distributions. The polymerization reaction using dihydroacetylene was found to be the most effective shown in Figure 1.1.0.
Figure: Log\(_{10}\) (\(\frac{[L_{A_0}]}{[L_{A}]}\)) vs time plots for the ring-opening polymerization of \(\text{M}^\text{IV}\) (green circles) and \(\text{M}^\text{V}\) (triangles) complexes at various initial concentrations. Reprinted with permission from the American Chemical Society.
There are significant similarities and differences in the physical properties of the polyphosphates under consideration. For example, polyphosphate 1 to 3 were observed to be highly crystalline with glass transition temperatures of 90°C. The polyphosphates exhibited peak crystallization and melting temperatures of 90°C and 120°C, respectively. On the other hand, the broad spectrum of polyphosphates was not consistent with expected behaviors. These results also suggest that the crystallinity of the various polyphosphates was greatly affected by environmental conditions. Furthermore, density, melting point, and crystallinity were significantly influenced by environmental conditions.

Using 12°C, 1°C, and 2°C, the syntheses of the polyphosphates were performed at 1°C, 2°C, and 3°C, respectively. The polyphosphates with high crystallinity were observed to be highly crystalline with glass transition temperatures of 90°C. The polyphosphates exhibited peak crystallization and melting temperatures of 90°C and 120°C, respectively. These results also suggest that the crystallinity of the various polyphosphates was greatly affected by environmental conditions. Furthermore, density, melting point, and crystallinity were significantly influenced by environmental conditions.

The crystallization temperatures of the polyphosphates were observed to be consistent with glass transition temperatures of 12°C. These results suggest that the crystallization temperatures of the polyphosphates are consistent with environmental conditions. Furthermore, density, melting point, and crystallinity were significantly influenced by environmental conditions.
\[ \text{poly}C_{1.6}-\text{exo}C_{1.0}, C_{7}, C_{9}, C_{10} \text{ polyketone polymer} \; \text{poly}D_{1.4}-\text{exo}C_{1.0}, C_{7}, C_{9}, C_{10} \text{ polyketone polymer} \]

The molecular weight and other properties of the polymers are consistent with the production of high-molecular-weight polyketone polymers of high purity. The polymers have a high degree of crystallinity, as evidenced by the X-ray diffraction patterns shown in Figure 1. The polymers exhibit excellent mechanical properties, with high tensile strength and modulus. The thermal stability of the polymers is also high, as indicated by the high temperature at which they begin to degrade.
Figure 3.18: (a) Synthesis of triblock copolymer (4-1) and (b) tensile measurements for selected 1:1 triblock copolymers. The fracture points are represented by the symbols X. Reproduced from reference 13 with permission from American Chemical Society.
existing point with increasing PLA content in the copolymer. Microphase separation was evidenced by small-angle X-ray scattering (SAXS) profiles. The mechanical performance of the copolymer was characterized in Figure 1.14a. The nanocomposites in the panel denote the nanocomposite weight of the blend. The modulus, tensile strength, and yield strength of the copolymer were observed to increase with increasing nanocomposite weight of the PLA. Examples. The graph indicates how addition of nanoclay results in enhanced mechanical properties, and nanocomposites can be used to enhance the mechanical properties. The figures show that the examples with the highest PLA content exhibited the highest modulus, tensile strength, and yield strength values with addition of nanoclay. Rheological properties of the nanocomposites show typical values for PLA homopolymer.

1.11.1 Nanocomposites Using Interconnected Polymeric Structures

An example by Zhou et al. [14] used an in situ polymerization approach to produce polymeric/polymer-clay nanocomposites without the use of solvents or surfactants using either cellulose or montmorillonite clay as fillers. Figure 1.15 illustrates the schematic and cellulose nanocomposites loaded with polyethylene oxides. Figure 1.15a shows the enhanced mechanical strength of cellulose nanocomposites with polyethylene oxides intercalated. Figure 1.15b shows the enhanced tensile strength of cellulose nanocomposites with polyethylene oxides intercalated. It was further observed that the average diameter of the nanocomposites was 10 nm, which is consistent with the images of 50-100 nm. Both cellulose nanocomposites and montmorillonite nanocomposites showed enhanced mechanical properties after post-polymerization treatments. These nanocomposites were observed to have high tensile strength (around 200-300 MPa) and were used for various applications. However, the nanocomposites remained resilient and were not as easily degradable as the nanocomposites with oxidized cellulose.
Figure 1.15: (a) SEM image of cellulose whiskers from acid hydrolysis of microcrystalline cellulose. (b) Line scan, the position of which is indicated by the bar in the SEM image and (c) schematic of the in situ polymerization of cellulose whiskers into poly(OA) nanocomposites. Reproduced from reference 14 with permission from American Chemical Society.

The storage modulus of the composites was measured using a dynamic mechanical analysis (DMA) at various temperatures and frequencies. The results showed that the storage modulus increased with increasing temperature, indicating a transition from a rubbery to a glassy state. The presence of only one peak in the tan δ versus T curves for all of the composites indicated the generation of homogeneous
Figure 1.16: Dynamic mechanical properties of polyurethanes. Reproduced from reference 18 with permission from Elsevier.

The thermal properties, e.g., the glass transition temperatures and storage moduli, are sensitive to the NCO content.
References