Macromolecules
EDITORIAL

Macromolecules **2009**, *42*, 7987–7989
DOI: 10.1021/ma902107w

A Virtual Issue of *Macromolecules*: "Polymers from Renewable Resources"

It is our pleasure to announce the second "virtual issue" for *Macromolecules*. A virtual issue collects a set of recently published *Macromolecules* papers in a Web-only edition of the journal; they may also be found directly from the *Macromolecules* Home Page (http://pubs.acs.org/page/mamobx/vi/2). We provide online access to these papers free of charge until the subsequent virtual issue and thus aim to broaden accessibility to a subset of the most exciting recent science in *Macromolecules*. We hope that this new initiative will be useful to the polymer science community and beyond. This virtual issue focuses on the synthesis of polymers from renewable resources. As fossil fuel resources dwindle, there is growing interest in developing new feedstocks for future polymers. There are important fundamental scientific issues that must be addressed to render these materials competitive with their petrochemical-based cousins, and the contributors to *Macromolecules* tackle many of the most important research questions. The topics covered by *Macromolecules* include the synthesis of new renewable monomers and the catalytic conversion of these and more established renewable monomers into their corresponding polymers. The design and development of renewable copolymers with various macromolecular architectures for enhanced properties is central to many of these efforts. Papers in *Macromolecules* also cover the synthesis and characterization of new polymers from naturally occurring materials such as cellulose and lignin. Below we highlight 17 papers that deal with this important contemporary area of polymer science and were published in *Macromolecules* in 2008 and the first half of 2009.

Foremost among these papers in this issue is a *Macromolecules* Perspective by Prof. Alessandro Gandini of the University of Aveiro that critically reviews the current state of the field of polymers from renewable resources.[1] Gandini provides a thought-provoking account on a wide variety of renewable resource polymers. He covers materials derived from starch, terpenes, vegetable oils, and other abundant agricultural feedstocks and provides a view based on a decades long history with renewable materials. This Perspective is recommended both for new researchers to the field and for those wanting to learn more about the diversity of research activities in the area of renewable polymers. At the end of this Perspective Gandini comments on the dwindling supply and high cost of petroleum feedstocks and states "It would therefore be particularly wise to prepare the future with a responsible strategy aimed at assessing the potential of both known and novel macromolecular materials through a more systematic and intense research program covering all aspects of their conception, characterization, and possible applications." The original research articles highlighted below are all contemporary examples of such important research efforts.

The development and polymerization of new monomers is central to the renewable polymer effort. Several polymerization mechanisms can be exploited, and one of contemporary interest is controlled radical polymerization. Mosnáček and Matyjaszewski describe the atom-transfer radical polymerization of the cyclic acrylate α-methylene-γ-butyrolactone or tulipalin, a natural product found in tulips (Figure 1).[2] Controlled polymerizations of this monomer were achieved, and block copolymers with other acrylates could be prepared. The polymer formed from the polymerization of tulipalin exhibits a high glass transition temperature and could be a useful component of renewable thermoplastic elastomers. Smith and Baker describe the synthesis of new monomers based on lactide, one of the most studied renewable monomers, in a pair of papers on substituted lactide derivatives. In the first, a thermoresponsive polylactide was prepared from a lactide monomer symmetrically substituted with oligo(ethylene glycol) units (Figure 2).[3] High molecular weight polymers could readily be prepared, and these materials exhibited tunable levels of hydrophilicity based on the length of the oligo(ethylene glycol) side chains. In some cases, the materials were shown to have a lower critical solution temperatures in water, and the authors emphasize their potential use as thermoresponsive polymers for biomedical applications. In a related approach to derivatized aliphatic polyesters, they synthesized a new reactive monomer containing alkynes and describe the synthesis and polymerization of "clickable" polyglycolides.[4] They were able to controllably polymerize propargyl-substituted glycolides (derived from the renewable glycolic acid) to give homopolymers and copolymers with lactide. These reactive polymers could then be modified by the copper(I)-mediated 1,3-dipolar cycloaddition of azides and alkynes—a now classical "click" reaction. Again, polymers with controlled hydrophilicity could be prepared by controlling the level and nature of the azide coupling partner. This paper highlights the importance of new monomer synthesis combined with the utility of click reactions[5] for the discovery and development of new functional materials with renewable content.

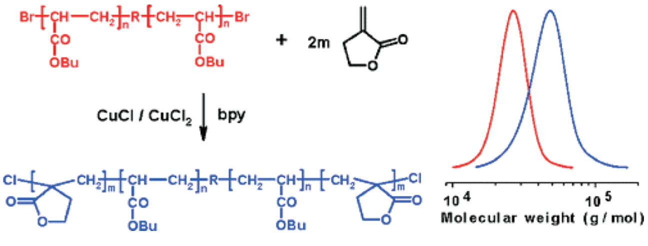

Figure 1. Atom transfer radical polymerization of tulipalin. From ref 2.

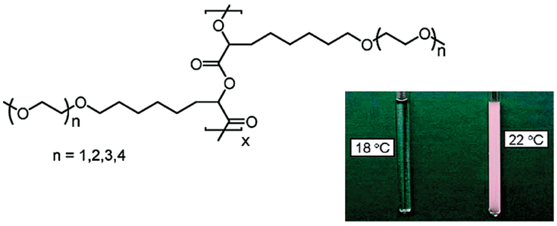

Figure 2. Water-soluble thermoresponsive polylactides. From ref 3.

There have also been several efforts in the design and synthesis of new copolymers and other architecturally diverse macromolecules from renewable monomers. In an effort to prepare toughened polylactide-based materials, Pitet and

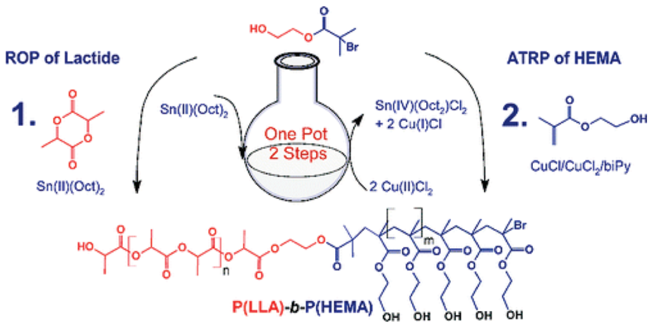

Figure 3. Poly(lactide)-*block*-poly(HEMA) block copolymers. From ref 7.

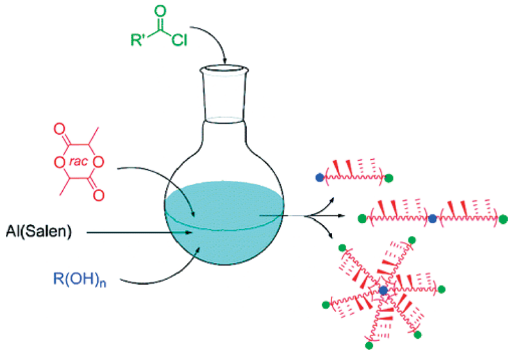

Figure 4. Synthesis of stereoregular, star-shaped poly(lactide). From ref 8.

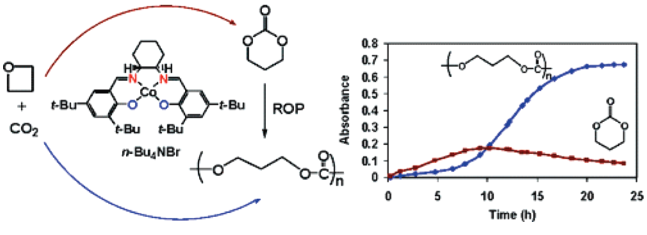

Figure 5. Catalysts for the coupling of CO_2 and oxetane. From ref 14.

Hillmyer demonstrated that, by combining ring-opening metathesis and cyclic ester polymerizations, new ABA polylactide triblock copolymers could be prepared with controlled molar mass and composition.[6] This work highlights the use multiple polymerization mechanisms to produce new hybrid macromolecules that contain renewable resource segments. Materials containing more than 90 wt % polylactide exhibited significantly enhanced toughness as compared to the parent homopolymer. In another example of combining polymerization mechanisms, Frey demonstrated that poly(hydroxyethyl methacrylate)-polylactide block polymers could be produced in one pot by a combination of ring-opening polymerization and atom transfer radical polymerization by using a "double-headed" initiator (Figure 3).[7] These new block polymers combine the degradable and renewable polylactide with biocomapatible poly(hydroxyethyl methacrylate) and represent one of the few examples of polyester-polyacrylate block copolymers. The authors emphasize the simplicity of their polymerization process and propose that these new amphiphilic block copolymers may have utility in drug delivery applications. Dove and co-workers utilized specifically end-functionalized polylactides to prepare a set of architecturally diverse macromolecules using a one-pot procedure (Figure 4).[8] Interestingly, these authors utilized aluminum complexes that gave heterotactic telechelic polylactides. Using various acid chloride end-capping reagents, the authors demonstrated that a range of reactive end groups could be incorporated at the polylactide chain termini. Specifically, both radical addition−fragmentation transfer agents and alkyne groups (for "click" chemistry) were installed for the controlled production of block and star-shaped polylactides. The authors highlight the enhanced stability of the telechelic polylactides toward degradation. The development of methods to produce cyclic polymers has received much attention in the literature, and the report by Kricheldorf and co-workers describes a simple method for the production of cyclic polylactides using only imidazole in a melt polymerization of lactide.[9] The authors probed the mechanism of cyclic formation and posit that an initial kinetically controlled ring-opening process yields even-numbered cycles, and equilibration of this mixture yields odd-numbered macrocycles by transesterification. Racemization of enantiomerically pure polylactides was also observed, and the authors provide an explanation based on reversible deprotonation of the polylactide backbone by imidazole. Mathers utilized naturally occurring monoterpenes D-limonene, limonene oxide, and β-pinene as chain transfer agents in the ring-opening metathesis polymerization of dicyclopentadiene.[10] The properties of the resultant soluble hyperbranched polymers could controlled by the choice of monoterpene. The authors demonstrate that this catalytic method is convenient for integrating renewable resource compounds into functional materials with tunable molecular characteristics.

Central to success in finding new ways to polymerize monomers derived from renewable resources is the development of new catalysts. A significant amount of work focuses on lactide, the cyclic diester of lactic acid. Williams and co-workers reported a series of discrete bis(thiophosphinic amido)yttrium complexes that exhibit excellent activity for the polymerization of racemic lactide.[11] Although not living, the initiators exhibited linear plots of number-average molecular weight versus the percentage conversion, close agreement between the theoretical and observed degree of polymerization, and a moderate level of heterotactic selectivity. Feijen, Chen, and co-workers have reported aluminum complexes ligated by a chelating bis(pyrrolidene) Schiff base framework that are living for lactide polymerization. The aluminum complexes polymerized (*S*,*S*)-lactide to highly isotactic PLA without monomer epimerization and yielded isotactic-biased polymer from *rac*-lactide as well as atactic polymer from *meso*-lactide.[12] Darensbourg et al. reported that tridentate Schiff base calcium derivatives are very effective catalysts for ring-opening polymerization of both lactides and trimethylene carbonate to produce high molecular weight homopolymers as well as random and block copolymers with low polydispersities.[13] Darensbourg and Moncada discovered that a (salen)Co(II) complex in conjunction with a n-Bu_4NBr cocatalyst forms a very active catalyst system for the ring expansion of oxetane with carbon dioxide to form trimethylene carbonate (Figure 5).[14] Subsequently, this monomer is polymerized to form the polycarbonate. In related work, Endo and co-workers reported the radical polymerization of glycidyl methacrylate with concurrent LiBr-catalyzed ring expansion of the glycidyl moiety with carbon dioxide. The carbonation degree was controlled by the choice of reaction conditions, allowing unreacted epoxide groups for subsequent transformations.[15]

The modification and use of naturally occurring polymers were emphasized by three groups. Pranger and Tannenbaum described the preparation of biobased polymer matrix nanocomposites by polymerizing furfuryl alcohol in the presence of

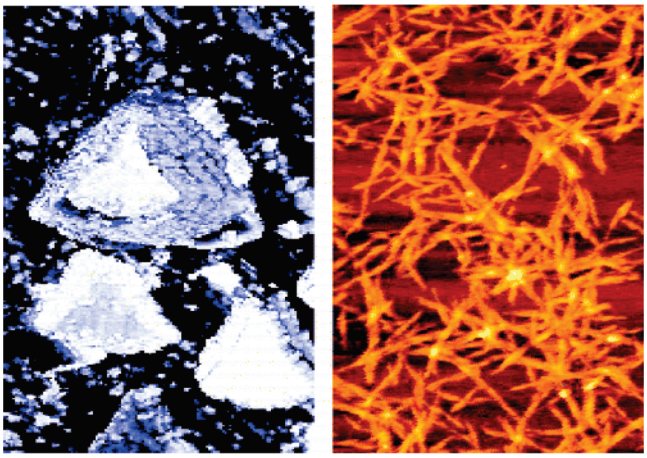

Figure 6. Biobased nanocomposites prepared by in situ polymerization of furfuryl alcohol. From ref 16.

both cellulose nanowiskers and montmorillonite clay.[16] In this work the cellulose nanocrystals have multiple functions (Figure 6). They serve as the dispersed phase of the nanocomposite, and the sulfonic acid residues on the surfaces of these particles act to catalyze the polymerization of furfuryl alcohol. The in situ polymerization is a convenient route to biobased nanocomposites with improved resistance to thermal degradation. The soluble cellulose derivative hydroxylpropyl cellulose was used by Malmström and co-workers to prepare an interesting set of water-soluble graft copolymers using a combination of ring-opening polymerization and atom transfer radical polymerization.[17] In this work the authors functionalized the hydroxyproyl cellulose first with polycaprolactone and then extended those graft chains with poly(acrylic acid) (through the *tert*-butyl-protected ester). These amphiphilic copolymers were explored as “nanocontainers” for the encapsulation of hydrophobic molecules. Iovine et al. explored the chemical modification of lignin, an abundant renewable polymer that is a byproduct of, among other things, the paper manufacturing process.[18] In this work the authors describe the formation of arylboronate ester derivatives using a mild dehydration process to give organic solvent-soluble materials. This approach enables the properties of lignin-containing materials to be tuned for various applications of these biobased materials.

Renewable resource polymers represent and active and growing area of polymer science. The articles summarized above highlight some important and interesting contributions to *Macromolecules* that provide the fundamental underpinnings for future technological development of these emerging materials.

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