

#### Block polyester copolymers by ring opening polymerization employing new catalysts (Ramot) code: 3-2016-1007

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Poly(lactic acid) (PLA) is a plastic material derived from annually-renewable resources, which decomposes post-consumption to non-toxic materials. PLA is produced by the catalyzed ring opening polymerization (ROP) of lactide.

PLA is attracting considerable current interest and has found various commodity (packaging, fibres, etc.) and biomedical (sutures, stents, tissue engineering, drug release) applications. Substantial worldwide effort is dedicated to the development of methodologies that would enable the fabrication of PLA block-copolymers of precise microstructures, since these are expected to be suitable for various advanced applications. Yet, the potential of PLA-based materials is far from being fully exploited, since the ability of the current technology to produce precise as well as sophisticated block-copolymers is limited. To date, the most advanced microstructural varieties of PLA are block-copolymers, such as stereo-diblock PLLA-PDLA, or PEG-PLLA that may offer higher tensile strength and melting temperature, or controlled rate of drug release, respectively.

Tools to tailor the properties of PLA by controlling the microstructure of multi block co-polymers of L-lactic acid, D-Lactic acid and other biodegradable polymers such as those of  $\square$ -caprolactone (CL) will greatly contribute to the production and use of biodegradable polymers.

Biodegradable polymers are expected to be a major player in fastening devices, Implants, Hygienic products, Drug delivery systems and others, in the coming years.

Improvements in toughness, heat resistance and bio composites will lead the PLA co-polymers to the next stage and establish its status in the market of bioplastics through expanding usage and penetration to additional market segments.

### The Invention

A novel Mg-based catalyst and method for ring opening polymerization (ROP) of cyclic esters such as lactide (LA), □-caprolactone (CL) and related monomers. The method is an easy "one-pot" process, is very fast, and enables the production of "tailor-made" block-copolymers of PLA and PCL including AB, ABA, ABC, ABCBA (and higher) microstructures (A, B, and C representing PCL, PLLA, PDLA blocks), with 'as-desired' block-lengths, and superior thermal properties. This in turn, allows for improved characteristics of these aliphatic polyesters, which are attracting high current interest, being derived from annually renewable resources on one hand, and being potentially degradable (compostable) post-consumption on the other hand

# The Technology

Poly(lactic acid) (PLA) is a biodegradable polymer prepared by the catalyzed ring opening polymerization of lactide. An ideal catalyst should enable a sequential polymerization of the lactide enantiomers to afford stereoblock copolymers with predetermined number and lengths of blocks. The invention includes a magnesium based catalyst that combines very high activity with a true-living nature, which gives access to PLA materials of unprecedented microstructures. The catalyst works on L-lactic acid lactide, D-lactic acid lactide and caprolactone.

Full consumption of thousands of equivalents of L-LA within minutes gave PLLA of expected molecular weights and narrow molecular weight distributions. Precise PLLA-b-PDLA diblock copolymers having block lengths of up to 500 repeat units were readily prepared within 7 min, and their thermal characterization revealed a stereocomplex phase only with very high melting transitions and melting enthalpies. The one pot sequential polymerization was extended up to precise hexablocks having 'dialed-in' block lengths. The capability of the catalyst to polymerize □-caprolactone (CL) and related monomers in addition to lactides enable the production of hitherto unattainable block co-polymers with tailor made blocks of rigid (PLA) and soft (PCL) units

## Applications

The technology will have significant impact on a wide array of applications from cheaper and more durable utensils and packages, to larger penetration in the automotive and HW markets, as well biomedical applications such as drug delivery, tissue engineering and bio-degradable bone implants.

### Advantages

- Using of nontoxic and bio-compatible metals based catalysts such as magnesium
- Method that leads to stereo-regular polymers of the desired stereo-type, and fine tuning of catalyst



performance by variations of the ligand structure and the metal

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