Synthesis and characterization of copoly(L-lactic acid-caprolactone) and its stereo-effect with poly D-lactic acid and biodegradability

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Abstract

Random copolymerizations of L-Lactide with ε-Caprolactone by ring opening polymerization reactions were carried out. A number of copolymers were formed and observed that any composition of copolymer can be formed by changing the feed ratio of the respective monomers. The effect of temperature and time in copolymerization reaction were studied. For their characterization, NMR, IR, DSC and GPC were measured. The stereo-effect of the lactic acid based biodegradable polymers and copolymers for improve thermo-mechanical properties were studied. The obtained copolymers also show stereo-effect like homopolymer. The biodegradability of obtained polymers, copolymers and stereocomplex were studied in three different biodegradation methods; e.g., Enzymatic method, Composting method and Activated Sludge treatment method; and compared to each other.

Key words : Random copolymerizations, Ring opening polymerization, Stereo-effect, Biodegradability

Introduction

Plastic is the most extensively used polymer in the world. Plastics are used extensively in packaging due to their outstanding physical, mechanical, and chemical properties (Hernandez, 2004). It is impossible to develop modern civilization without plastic. Almost all commercial products must be packaged in plastic (Kelly, 1997). Because plastic packaging provides excellent protection of the product (Sinclair, 1995); it is almost nonreactive, it prevents products from air and moisture, it is very cheap to manufacture and it seems to last for a long time. Lasting for a long time, however, is now creating a major environmental problem after depositing in the atmosphere (Maneka Gandi, 2010). Another problem is that the traditional plastics are manufactured from non-renewable resources such as mineral oil, coal and natural gas, which enhances global warming (Bruno Gervet, 2007). Plastic Waste is more dangerous than Global Warming (Blair Coursey, 2003).

At present, biobased biodegradable polymers are the demand of times (Leaversuch, 2002). Among all the biobased biodegradable polymers, PLLA (poly L-lactic acid) is the most common and most widely used polymer because of its ease of preparation and excellent physical and mechanical properties (Luc Averous, 2009).

It is thought to be key component for the replacement of petrochemical based polymer products. Hence, a lot of experiments on this polymer already have been done (Yoshiharu Kimura, 2009; Courgneau, 2004). But still the polymer has some limitations in its mechanical and thermal properties; which are as- the mechanical properties, it has strong tensile strength value but the elongation at break is much smaller, and its resistance to heat is often around 100°C in spite of its high melting temperature (178°C) (Kawasaki, 1998). Moreover, PLLA is well known for its biodegradability (Avella, 2001; Karlsson, 1998), but its lack-adasisal biodegradation is hard to deal. To improve its brittle properties and biodegradability, random copolymerization is one of the expected approaches (Kylma, 1997), and lots of comonomers Lactones, Glycidol, etc. are being studied. Suppression of crystallinity results in flexible properties and excellent biodegradation (Fritz, 2001). Implementation of additives is also a good approach in this regards (Nadia Ljungberg, 2003; Ljungberg, 2005).
In this experiment, we have synthesized some copolymer of L-Lactic acid and ε-Caprolactone at different ratio; studied the thermal and mechanical properties of the copolymers and also studied the effect of their stereocomplex with poly D-lactic acid and their Biodegradation in different medium e.g., Composting, Enzymatic and Activated Sludge treatment method.

**Materials and Methods**

Synthesis of polymers from the monomers D-lactide, L-lactide and ε-Caprolactone and copolymers of L-lactide and ε-Caprolactone of different compositions were carried out in the presence of tetraphenyl tin as an initiator.

**Reagents**

L-lactide (LLA) and D-lactide (DLA) were purified by recrystallization from dried toluene under nitrogen atmosphere and then dried for 24 h under vacuum at 30°C. ε-Caprolactone (CL) (Boehringer Ingelheim) was purified by distillation under reduced pressure and treated with sodium sulfate to remove any residual moisture traces. Tetraphenyl tin and magnesium ethoxide (Wako Chemicals, Japan) was used as an initiator without purification. The enzymes for the biodegradation tests were Proteinase-K, Standard Activated Sludge provided from National Inst. Tech. Eval., Japan and compost from (Natural Compost Ltd.) were collected and used directly after checking moisture content.

**Synthesis**

The polymers and copolymers were synthesized from their respective monomers. The polymerization reaction was carried out with L-lactide and ε-Caprolactone monomers (Kawasaki, 1998; Nijenhuis, 1992; Tasaka, 2001). The monomers/comonomers and tetraphenyl tin initiator (0.3 mol% versus total monomers) were charged on a dried two necked flask. The flask was sealed with air condenser and moisture trap and heated at 130 ± 10°C for 3 days. They were allowed to cool down to room temperature and the contents were dissolved in chloroform after the addition of a few drops of methanol to stop the polymerization reaction. Some of the crude polymer was obtained as a precipitate in excess methanol, and was purified by repeated precipitations. Then they were dried in a vacuum dryer at 50°C for 24 h. A series of copolymers with different compositions were synthesized by changing the feed molar ratio of LLA/CL from 0/100 to 100/0.

**Measurement**

**Nuclear magnetic resonance spectroscopy**

$^1$H NMR (500MHz) and $^{13}$C NMR (125MHz) spectra were recorded on a JEOL JNM A-500 spectrometer. The spectra were mainly obtained chloroform-d solutions at room temperature with tetramethylsilane (TMS) as internal standard (Espartero, 1996).

**Fourier-transform infrared spectroscopy**

The Infrared (IR) spectra were recorded on a Nicolet 710 FT-IR spectrometer. The samples were recorded using films casted on a potassium chloride plate from chloroform solutions (Kawasaki, 1998).

**Gel permeation chromatography**

The molecular-weight distributions ($M_n$, $M_w$ and polydispersity indices) were measured with GPC (Tosoh, model HLC-8020) using polystyrene standards in chloroform solvent. The columns were TSK gel G4000HXL and a TSK gel G3000HXL with a limited exclusion molecular weight of 4x10^5. The eluent was CHCl$_3$ and the flow rate was 0.6 ml/min (Huh, 1999; Hyon, 1997).

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![Fig. 1: Polymerization scheme](image)
**Thermal analysis**

The thermal behavior of the polyesters was studied by using a differential scanning calorimeter (DSC, model-10A) connected with a chart recorder and a temperature control unit (PTC 10D, Rigaku). The heating rate was 10°C/min and an empty aluminum pan was used as reference. The glass transition temperature \( T_g \) was determined as the lower flexion point of the recorded step change in heat capacity, and melting points \( T_{m1}, T_{m2} \) were defined as the peaks of the endotherm curve (Ljungberg, 2005; Kawasaki, 1998).

Samples of 3-8 mg (weighed into aluminum pans) were measured from -50°C to 250°C at a heating rate of 10°C/min.

**Biodegradation**

**The Biodegradability was evaluated in three different methods**

a. Enzymatic hydrolysis test
b. Compost degradation test and
c. Activated Sludge test

**Enzymatic hydrolysis**

Polyester samples (20 ± 0.5mg) and 5 ml phosphate buffer (NaH₂PO₄/Na₂HPO₄, pH=7.00) were added to each of the four tubes. Then 100 units of enzyme Proteinase-K were added into two of the each tubes and other two were for blank test. The test was carried out at 37°C for 24 h. After filtration (0.2 µm membrane filter) TOC (total organic carbon) was measured. The TOC values were corrected appropriately by subtracting the blank levels (Li, 1996; Kawasaki, 1998).

**Compost degradation test**

The standard compost was supplied by the company. The moisture content of the compost is 63 ± 2%. A small piece of sample is kept at the centre of the compost in a digester and the digester is kept in a closed vessel with excess water so that its inside become saturated by moisture. Then the whole vessel is kept in an oven at 60°C for 15 days. Then the biodegradation is calculated by the percent weight loss (Karlsson, 1998).

**Activated Sludge test**:

In this test method the sample (30±0.3 mg) is digested in Activated Sludge in a controlled buffer medium (KH₂PO₄, K₂HPO₄, and Na₂HPO₄,2H₂O; pH=7.00 and stabilizers NH₄Cl, MgSO₄.7H₂O, CaCl₂ and FeCl₂.6H₂O in distilled water). Activated Sludge and Buffer solution ratio in digester is 1:10. The test is carried out at 27°C for 60 days. The sample is digested to CO₂, which is absorbed by CaCl₂ as a result O₂ is consumed inside the digester and Biodegradation is calculated from the ml of O₂ consumed (Kawasaki, 1998).

**Results and Discussion**

**Synthesis and characterization of polymers and copolymers**

The homopolymers of L&D-Lactic acid and ε-Caprolactone and copolymers of L-Lactic acid and ε-Caprolactone molar feed ratio 90:10, 50:50 and 10:90 were obtained by ring-opening polymerization (ROP) reaction using Tetraphenyl tin as a catalyst. The product composition can be controlled by varying the feed ratio of monomers at a definite reaction.

<table>
<thead>
<tr>
<th>Feed ratio</th>
<th>Product Composition</th>
<th>Catalyst</th>
<th>Temp.</th>
<th>Time (H)</th>
<th>Yield</th>
<th>( M_n )</th>
<th>( M_w )</th>
<th>( M_w/M_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA=100</td>
<td>100</td>
<td>Sn(Ph)₄</td>
<td>125</td>
<td>46</td>
<td>94.44</td>
<td>98781</td>
<td>141156</td>
<td>1.43</td>
</tr>
<tr>
<td>PLLA=100</td>
<td>100</td>
<td>Sn(Ph)₄</td>
<td>135</td>
<td>72</td>
<td>96.82</td>
<td>106695</td>
<td>167824</td>
<td>1.57</td>
</tr>
<tr>
<td>PDLA=100</td>
<td>100</td>
<td>Sn(Ph)₄</td>
<td>125</td>
<td>42</td>
<td>94.58</td>
<td>56186</td>
<td>67423</td>
<td>1.12</td>
</tr>
<tr>
<td>PDLA=100</td>
<td>100</td>
<td>Sn(Ph)₄</td>
<td>140</td>
<td>62</td>
<td>98.35</td>
<td>90595</td>
<td>151294</td>
<td>1.67</td>
</tr>
<tr>
<td>LA:CL=90:10</td>
<td>90.5/9.5</td>
<td>Sn(Ph)₄</td>
<td>130</td>
<td>70</td>
<td>94.00</td>
<td>107929</td>
<td>158656</td>
<td>1.47</td>
</tr>
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<td>LA:CL=50:50</td>
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<td>Sn(Ph)₄</td>
<td>130</td>
<td>72</td>
<td>91.36</td>
<td>93110</td>
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<td>1.41</td>
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<tr>
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<td>Sn(Ph)₄</td>
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<td>70</td>
<td>89.87</td>
<td>80536</td>
<td>110334</td>
<td>1.37</td>
</tr>
<tr>
<td>PCL=100</td>
<td>100</td>
<td>Sn(Ph)₄</td>
<td>125</td>
<td>98</td>
<td>85.70</td>
<td>34292</td>
<td>60010</td>
<td>1.75</td>
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</table>
condition. The polymerization reaction is highly temperature sensitive. Minimum 120°C temperature is required for obtaining a satisfactory lower molecular weight (M_n-10,000 min.) polymer and 130-135°C temperature gives a satisfactory higher molecular weight (M_n-1,50,000 min.) polymer. Temperature higher than 140°C shortens the reaction time by 12-24 hrs but yellowing of the product is occurred.

The effect of time in polymerization reaction is also significant. Low time gives lower molecular weight polymer and higher time gives higher, but very high time and temperature gives yellowing of the product and then burns. The polydispersity (M_w/M_n) also depends on the temperature and time. At moderate temperature and time (130-135°C and 72hr.) the polydispersity is satisfactory. At this temperature and time the product yields are also higher (around 85-95%).

**Mechanical properties**

After formation of film, from the obtained polymers by solvent casting method in chloroform solvent, the tensile strength and elongation properties are observed. The higher molecular weight polymer shows higher tensile strength properties. Molecular weight doesn't show any influence in elongation properties. In presence of a small amount (about 10%) of Caprolactone the L-Lactic acid and Caprolactone copolymers shows high tensile strength and very high elongation properties.

At very high amount (up to 90%) of Caprolactone content, the tensile strength and elongation properties gradually decrease. At this composition the TS value is even less than pure PLLA but the elongation property is improved.

**Thermal properties**

From the Differential Scanning Calorimetry (DSC) analysis the melting temperature (T_m) of PLLA and PDLA are around 180°C and ΔH is around 50 J, but in case of second heating the T_m is decreased slightly (by 5-10°C). In case of PCL the T_m is 67°C having no glass transition temperature (T_g) and in second heating it is decreased to 56°C, but another T_m value shows at 32°C. The presence of caprolactone in PLLA copolymer, T_m is decreased significantly and with the increase of its percentage the value decrease gradually. The presence of caprolactone in copolymer eliminates the T_g of L-Lactic acid (Table II).

**Stereo-effect**

To study the stereoeffect of the obtained homopolymer (PLLA) and copolymers (PLLA:CL) the film of the blends were obtained by solvent casting method of dissolving the polymer and copolymers at a ratio of 50:50 (by wt.) in chloroform solvent.

![Fig. Tensile strength and elongation at break curve of polymers](image)
From the DSC of the obtained blend films it is clear that the blends form stereocomplex perfectly at any composition of caprolactone in copolymer. The $T_m$ value increased by about $50^\circ$C in all cases but does not show second $T_m$. The tensile strength and percent elongation also increased significantly except TS at 90% CL.

### Table II: Thermomechanical properties of polymers and copolymers

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mw</th>
<th>TS</th>
<th>% El</th>
<th>1st Tg</th>
<th>1st Tm</th>
<th>1st $\Delta H$</th>
<th>2nd Tg</th>
<th>2nd Tm</th>
<th>2nd $\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA=100</td>
<td>141156</td>
<td>24.10</td>
<td>6.53</td>
<td>111.2</td>
<td>179.9</td>
<td>45.81</td>
<td>-</td>
<td>176.2</td>
<td>51.38</td>
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<tr>
<td>PLLA=100</td>
<td>167824</td>
<td>31.44</td>
<td>6.47</td>
<td>112.1</td>
<td>179.8</td>
<td>51.12</td>
<td>-</td>
<td>176.1</td>
<td>56.33</td>
</tr>
<tr>
<td>PDLA=100</td>
<td>67423</td>
<td>41.62</td>
<td>15.30</td>
<td>115.5</td>
<td>179.3</td>
<td>54.20</td>
<td>-</td>
<td>171.7</td>
<td>51.12</td>
</tr>
<tr>
<td>PDLA=100</td>
<td>151294</td>
<td>45.38</td>
<td>15.40</td>
<td>116.2</td>
<td>179.8</td>
<td>52.23</td>
<td>-</td>
<td>171.3</td>
<td>47.18</td>
</tr>
<tr>
<td>LA:CL=90.5/9.5</td>
<td>158656</td>
<td>40.45</td>
<td>450.47</td>
<td>151.2</td>
<td>-</td>
<td>13.19</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LA:CL=52.3/47.7</td>
<td>131283</td>
<td>21.23</td>
<td>145.73</td>
<td>-</td>
<td>148.3</td>
<td>12.67</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LA:CL=7.7/92.3</td>
<td>110334</td>
<td>10.51</td>
<td>44.67</td>
<td>-</td>
<td>142.7</td>
<td>12.45</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PCL=100</td>
<td>60010</td>
<td>21.86</td>
<td>11.50</td>
<td>-</td>
<td>67.4</td>
<td>89.95</td>
<td>31.7</td>
<td>62.77</td>
<td>55.9</td>
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</table>

### Table III: Stereo-effect of copolymers

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ratio with PDLA</th>
<th>TS</th>
<th>% El</th>
<th>1st Tg</th>
<th>1st Tm</th>
<th>1st $\Delta H$</th>
<th>2nd Tg</th>
<th>2nd Tm</th>
<th>2nd $\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA=100</td>
<td>50-50</td>
<td>60.86</td>
<td>104.73</td>
<td>-</td>
<td>237.6</td>
<td>65.06</td>
<td>-</td>
<td>232.8</td>
<td>86.31</td>
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<tr>
<td>LA:CL=90.5/9.5</td>
<td>50-50</td>
<td>44.06</td>
<td>333.47</td>
<td>-</td>
<td>206.5</td>
<td>34.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LA:CL=52.3/47.7</td>
<td>50-50</td>
<td>22.58</td>
<td>123.62</td>
<td>-</td>
<td>206.2</td>
<td>26.81</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LA:CL=7.7/92.3</td>
<td>50-50</td>
<td>6.88</td>
<td>32.93</td>
<td>-</td>
<td>204.6</td>
<td>22.96</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Biodegradation

In Enzymatic biodegradation the copolymer of ratio LL:CL=90:10 shows highest biodegradation in all powder, film and stereocomplex forms. 90% Lactic acid content copolymer shows highest biodegradation. Among the three forms the powder form shows highest biodegradation (about 30% in 24 hrs.) then film form (about 15% in 24 hrs.) and the stereocomplex form is the least (about 3% in 24 hrs.). With the increase of CL% the value decreased gradually.

In case of Activated Sludge Biofegradation higher percentage of CL content copolymers show higher biodegradation-in all three forms. 8% Lactic acid containing copolymer shows the highest biodegradation. The powder form shows the highest biodegradation (about 55% in 60 days), then stereocomplex form (about 20% in 60 days) and then the film form is the least (about 3% in 60 days). With the increase of LA% the value decreased gradually.

In Compost Biodegradation method the degradation rate is increased first rapidly then gradually with the increase of CL percentage and pure PCL has the highest value (about 90% in 15 days). The stereocomplexes also show steady and gradually increased biodegradation rate with the increase of caprolactone percentage. But the highest biodegradation value shows the copolymer of less lactic acid content, not any of the pure polymers.

Conclusion

Copoly(LLA/CL)s were synthesized from the two different kinds of monomers. One is biomonomer and another is non-biromomers both has biodegradibility. L-lactic acid, which can be produced from important bioresources, glucose and plant oil. These two monomers can be polymerized in any
composition and composition can be controlled by changing feed ratio. Copolymers containing less percentage of caprolactone show high mechanical and thermal properties. The mechanical and thermal properties also can be improved by the formation of stereocomplex and all the compositions of L-Lactic acid and caprolactone copolymers form a stereocomplex with poly D-Lactic acid. The higher lactic acid content copolymers show high enzymatic biodegradability because enzymes are very sensitive to compounds. On the other hand in Activated Sludge and Composting biodegradation methods show higher biodegradability at higher percentage of caprolactone containing copolymers. Because Activated Sludge and Compost provides versatile microorganism seeds at the test.

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