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Research Article

**NOVEL SYNTHESIS OF PLASTICIZERS OF POLY  
(L-LACTIDE) BIOPLASTIC FILMS AND THERE THERMAL  
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**Abstract:**

*Liquid star-shaped  $\epsilon$ -caprolactone (CL) oligomers were synthesized by ring-opening reaction of CL using a six terminal hydroxyl group initiator, Boltorn<sup>®</sup> H2004, for use as new plasticizers of poly(L-lactide) (PLA) films. The Boltorn-CL oligomers containing two and four units of CL on each oligomer arm were prepared. The PLA/oligomer blend films were prepared by solution blending before film casting. A phase separation led to the formation of plasticizer droplets.*

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## INTRODUCTION:

Poly(L-lactide) (PLA), one of the most important bioplastics, has attracted increasing attention as a candidate for use in many application fields, such as tissue scaffold, drug delivery systems, packaging films and so on, because of its renewability, biodegradability, biocompatibility, good processability and good mechanical properties [1-4]. However, the low elongation at break and the high modulus of the PLA films have limited applications in packaging situations.

The flexibility of PLA films can be improved either by copolymerization [5,6] or by plasticizer blending [7]. The plasticizer blending is more convenient, more efficient, lower cost and faster compared to copolymerization. Low molecular weight plasticizers, such as citrate esters, significantly reduce the  $T_g$  and obviously improve the elongation at break of the PLA films [8,9]. However, the migration of these plasticizers from the PLA film matrix to the film surface due to their high mobility increases the  $T_g$  and reduces the film drawability with aging, which is the main problem [6,10]. High molecular weight plasticizers, such as poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG), were then investigated for plasticizing of PLA films to decrease the migration of plasticizers on aging [11-14]. However, the high molecular weight plasticizers usually induce phase separation in the PLA film matrices. It has been reported that tiny pools of liquid plasticizers, such as PPGs, are dispersed in the PLA film matrices and may locally plasticize PLA during plastic flow and have better effects on drawability than the crystallizable plasticizers such as PEGs [13,14]. The PPGs have also been shown to give efficient plasticization to improve the flexibility of the PLLA. Semi-crystalline poly( $\epsilon$ -caprolactone) (PCL) is a flexible biodegradable polyester due to its very low  $T_g$  (around  $-60^\circ\text{C}$ ). The five methylene units of the CL units induce high chain mobility and low  $T_g$ . PCL and CL oligomers have been investigated as biodegradable plasticizers [15-17]. However, to the best of our knowledge, the plasticization effect of star-shaped CL oligomers on PLA films has not been reported so far.

Thus, this paper describes the synthesis of liquid CL oligomers with 6-arm star-shaped structures for plasticizing PLA film. Effects of the CL chain length (two and four units) on each arm and plasticizer blend ratios (5 – 20 wt%) on the phase separation, thermal properties and mechanical properties of the PLA blend films were evaluated<sup>18-21</sup>. The PLA films blended with the 6-arm initiator, Boltorn<sup>®</sup> H2004, were also prepared for comparison.

## MATERIALS AND METHOD:

The poly(L-lactic acid) (PLA) was synthesized in our research unit at Mahasarakham University by ring-opening polymerization of a L-lactide monomer in bulk at  $165^\circ\text{C}$  for 2.5 h under a nitrogen atmosphere using 0.01 mol% stannous octoate (95%, Sigma) and 0.14 mol% 1-dodecanol (98%, Fluka) as the initiating system. The obtained PLA was granulated before drying in a vacuum at  $110^\circ\text{C}$  for 2 h to remove any un-reacted lactide. The intrinsic viscosity ( $[\eta]$ ) and viscosity-average molecular weight ( $M_v$ ) of the PLA were determined in chloroform at  $25^\circ\text{C}$ , and they were 2.53 dL/g and 104,700 g/mol, respectively. The  $\epsilon$ -caprolactone (CL, 99%, Acros Organics) monomer was purified by distillation under reduced pressure before use. A liquid fatty acid modified dendritic polyol with six terminal hydroxyl groups, trade name Boltorn<sup>®</sup> H2004, with a molecular weight of 3,100 g/mol (Perstrop) was used without further purification. All reagents used were analytical grade.

### Synthesis of CL oligomers

The CL oligomers were synthesized by ring-opening polymerization of the CL monomer in bulk at  $145^\circ\text{C}$  for 24 h under a nitrogen atmosphere using 0.04 mol% stannous octoate and Boltorn<sup>®</sup> H2004 as the initiating system. The resulting oligomers were purified by heating at  $110^\circ\text{C}$  under a vacuum for 6 h to remove un-reacted CL monomer. The CL monomers with two and four units were reacted at the hydroxyl end-groups of the Boltorn<sup>®</sup> H2004, giving Boltorn-2CL and Boltorn-4CL, respectively.

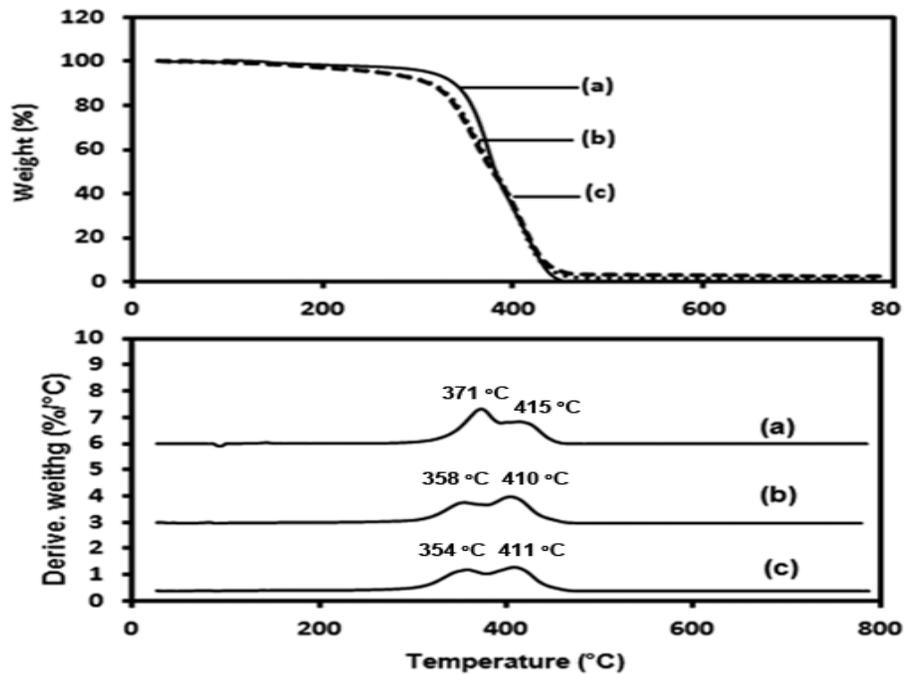
## RESULTS AND DISCUSSION:

### Characterization of CL oligomers

The yields of the CL oligomers measured by the evaporation of un-reacted CL were higher than 90%. Both the Boltorn-2CL and the Boltorn-4CL were liquid at room temperature, similar to the initiator, Boltorn<sup>®</sup> H2004. The  $M_n$  and MWD of the Boltorn<sup>®</sup> H2004 obtained from GPC were 2,600 g/mol and 1.5, respectively. The GPC curves of both the Boltorn-2CL and the Boltorn-4CL were of the unimodal type with the MWDs being 1.6 and 1.8, respectively. The  $M_n$ s of the CL oligomers from the GPC method were higher than the Boltorn<sup>®</sup> H2004 and increased with the CL units. The  $M_n$ s of the Boltorn-2CL and the Boltorn-4CL were 3,000 and 3,500 g/mol, respectively. The GPC results indicated that the CL monomers were connected to the Boltorn<sup>®</sup> H2004 molecules. CL oligomers with different CL chain lengths can be prepared.

**Table 1: Thermal transition properties of neat PLA and PLA blend films from the 2<sup>nd</sup> heating scan DSC thermograms.**

| PLA/plasticizer ratio (w/w) | T <sub>g</sub> (°C) | T <sub>c</sub> (°C) | T <sub>m</sub> (°C) | X <sub>c</sub> (%) |
|-----------------------------|---------------------|---------------------|---------------------|--------------------|
| Neat PLA film               | 55                  | 100                 | 175                 | 28.6               |
| PLA/Boltorn blend films     |                     |                     |                     |                    |
| 95/5                        | 51                  | 98                  | 174                 | 27.6               |
| 90/10                       | 50                  | 97                  | 174                 | 26.6               |
| 80/20                       | 47                  | 94                  | 173                 | 21.2               |
| PLA/Boltorn-2CL blend films |                     |                     |                     |                    |
| 95/5                        | 51                  | 99                  | 174                 | 19.3               |
| 90/10                       | 50                  | 98                  | 173                 | 23.5               |
| 80/20                       | 49                  | 95                  | 173                 | 42.9               |
| PLA/Boltorn-4CL blend films |                     |                     |                     |                    |
| 95/5                        | 53                  | 99                  | 173                 | 17.6               |
| 90/10                       | 49                  | 97                  | 173                 | 23.9               |
| 80/20                       | 48                  | 94                  | 172                 | 49.8               |

**Fig 2: TG (above) and DTG (below) thermograms of (a) Boltorn® H2004, (b) Boltorn-2CL and (c) Boltorn-4CL.**

The chemical structures of the CL oligomers were determined from  $^1\text{H-NMR}$  shows the  $^1\text{H-NMR}$  spectra of the CL oligomers including the peak assignments. The peaks of a – e were assigned to the methylene protons ( $-\text{CH}_2-$ ) of the CL units [21]. The peaks of f and g were assigned to the methylene ( $-\text{CH}_2-$ ) and methyl ( $-\text{CH}_3$ ) protons at the outer structure of the Boltorn units, respectively [22]. Meanwhile the peaks of f' and g' were assigned to the methylene ( $-\text{CH}_2-$ ) and methyl ( $-\text{CH}_3$ ) protons at the inner structure of the Boltorn units, respectively [22]. The  $^1\text{H-NMR}$  results confirm that the Boltorn-CL oligomers consisted of both the Boltorn and the CL characters. It should be noted that the peak area ratio of the CL/Boltorn units such as area ratio of peak a/peak f + f', increased as the CL units increased from two to four units in each arm. The  $^1\text{H-NMR}$  results support that the CL units increased with the initial CL feed ratio.

From the DSC analysis (DSC thermograms not shown), both the 1<sup>st</sup> and the 2<sup>nd</sup> heating scans did not exhibit the  $T_m$  of the CL crystalline. The CL sequences with two and four units of the Boltorn-2CL and the Boltorn-4CL, respectively, could not be crystallized. They are liquid at room temperature.

Figure 1 shows the thermogravimetric (TG) and derivative TG (DTG) thermograms of the Boltorn<sup>®</sup> H2004 and the CL oligomers from the TGA analysis. From the TG thermograms, the initial decomposition temperatures ( $T_{0s}$ ) of the Boltorn<sup>®</sup> H2004 and the CL oligomers were approximate 300 °C and 250 °C, respectively. This may be due to the CL chains reducing the intermolecular forces of the Boltorn<sup>®</sup> H2004 molecules. From the DTG thermograms, the hyperbranched Boltorn<sup>®</sup> H2004 showed two  $T_{d, \max}$  values at 371 °C and 415 °C that may be attributed to the decomposition of its outer and inner structures. The thermal stability changes of the CL oligomers can be clearly observed from the DTG thermograms. Both the  $T_{d, \max}$  values of the Boltorn cores slightly decreased as the CL units were added and increased. Then the thermal stability of the CL oligomers was a little lower than the Boltorn<sup>®</sup> H2004.

### CONCLUSION:

The phase separation between the PLA and plasticizer phases can be clearly observed as the formation of emptied voids in the SEM images of their fractured surfaces. These emptied voids were the tiny pools of liquid plasticizer. The phase separation increased (sizes of tiny pools increased) with the plasticizer blend ratio. However, both the PLA/Boltorn-CL blend films showed less phase separation than the PLA/Boltorn<sup>®</sup> H2004 blend film.

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