

## An Oligolactide Acrylate for UV-Curable Screen Printing Inks

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**Abstract:** Oligolactide diols (OL-OHs) were synthesized by ring opening reaction of L-lactide with 1,6-hexanediol (HD) at 160°C for 3 h. The amount of HD was varied in order to obtain low molecular weight OL-OHs. An Oligolactide Acrylate (OL-A) was then synthesized by functionalizing an OL-OH with acrylic acid at 130°C for 16 h. OL-OHs and the OL-A were characterized by <sup>1</sup>H-NMR, FTIR and GPC. The viscosities of OL-OHs were measured by Brookfield viscometer. <sup>1</sup>H-NMR and FTIR results confirmed that OL-OHs were synthesized successfully from lactide and HD as starting materials. It was found that an increase in the HD amount led to lower molecular weight OL-OHs having lower viscosity. The <sup>1</sup>H-NMR and FTIR results of the OL-A indicated that the OL-OH was functionalized with acrylic acid. A screen printing ink was formulated from the OL-A. Cured ink film achieved by UV curing was characterized by FTIR. In addition, adhesion of the obtained OL-A-based ink on various substrates was comparable with an ink made from commercial polyester acrylate.

**Key words:** Oligolactide diols, acrylation, UV-curable inks, viscosity, molecular

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### INTRODUCTION

Oligomers are the main components of UV-curable screen printing inks. The structures of the oligomers are based on acrylate esters which have high reactivity toward free radical polymerization, low oxygen inhibition and tendency to terminate by combination (Wicks *et al.*, 1999). Acrylate oligomers are manufactured at the expense of depleting petroleum resources and there has been an increase in the demand for environmentally friendly products. Therefore, comprehensive research has been conducted on acrylate oligomers which are derived from renewable resources such as vegetable oil as an alternative. For example, an epoxy acrylate oligomer has been synthesized from epoxidized soybean oil and from an epoxidized soy-methyl ester (Habib and Bajpai, 2011; Rengasamy and Mannari, 2013). A waterborne UV/air dual-cure polyurethane dispersion has also been synthesized from modified linseed oil (Chang and Lu, 2013). These studies show that such oligomers can be used to produce high performance, environmentally friendly coatings. However, vegetable oil-based acrylate oligomers are yellow in color and prone to be yellowing in the environment because of unsaturated double bonds in the molecular structure (Chang and Lu, 2013). Consequently, they are not suitable to be used for weather-resistant coatings.

Poly(lactide) (PLA) is a polymer produced from renewable resources. It has environmental benefits such

as requiring little energy for production and reducing the emission of VOCs (Sin *et al.*, 2012). PLA is a biodegradable polymer made from a non-toxic, naturally occurring lactic acid. Lactic acid-based polymers have been widely studied in environmental, medical and pharmaceutical applications due to their biocompatibility and biodegradability.

Oligomers of PLA are also found to be useful as curable materials. A number of studies have been done on the synthesis of methacrylate and acrylate lactide oligomers which can be thermal or UV cured through their unsaturated double bonds. In addition, Oligolactide Acrylates (OL-As) can be produced by the acrylation of Oligolactide diols (OL-OHs).

Low-molecular weight OL-OHs can be synthesized by the condensation reaction of lactic acid with polyols (Hiltunen *et al.*, 1997; Vasafi *et al.*, 2012; Liu *et al.*, 2013). However, there are several disadvantages; for example, it is difficult to remove the esterification by products from the reaction mixture in order that the reaction can be driven forward. Moreover, it requires high temperature and long reaction time. Glycolysis of PLA polymers with glycols is an alternative in which PLA resin is glycolyzed to produce hydroxyl-terminated oligomers (Tounthai *et al.*, 2013). OL-OHs can also be prepared via ring opening reaction of lactides with polyol ring openers in the presence of stannous octoate catalyst (Helminen *et al.*, 2001). This reaction requires no removal of by-products, lower reaction temperature and shorter reaction time.

The acrylation of OL-OHs can be performed with functionalizing agents such as acrylic acid, acryloyl chloride and isocyanate containing acrylate moiety. Of these, acrylic acid is the most widely used in commercial manufacturing process (Kulkarni *et al.*, 2013). The acrylation of OL-OHs with acrylic acid has been conducted in the presence of a catalyst, a polymerization inhibitor under azeotropic distillation.

Most OL-As are solid or highly viscous at room temperature. Reactive monomers must be included in the curable formulation so that it can be applied and cured at room temperature (Helminen *et al.*, 2002). Furthermore, the higher the amount of polyols, the lower the molecular weight of OL-OHs (Vasafi *et al.*, 2012). This results in less viscous OL-As which enable application in UV-curable screen printing inks which no study has yet investigated.

Therefore, the purpose of this research was to synthesize and characterize an oligolactide acrylate. Low-molecular weight OL-OHs were synthesized by ring opening reaction of L-lactide with 1,6-hexanediol. Then, an OL-A was produced by functionalizing an OL-OH with acrylic acid. To evaluate the potential use of the obtained OL-A in UV-curable application, a screen printing ink made from the OL-A was formulated and its adhesion on various substrates was also determined.

## MATERIALS AND METHODS

Puralact B3, L-lactide was kindly provided by Purac (Thailand) Ltd. (Rayong, Thailand). 1,6-Hexanediol (HD), tin(II) 2-ethylhexanoate (stannous octoate), acrylic acid (AA), p-Toluenesulfonic Acid Monohydrate (p-TSA) and tert-butylhydroquinone (DBHQ) were purchased from Sigma Aldrich (Missouri, United States). 1,6-hexanediol diacrylate (HDDA) and 2-hydroxy-2-methyl-1-phenylpropanone (IHT-PI 1173) were purchased from Innovachem Co., Ltd. (Bangkok, Thailand). Sartomer CN736 was purchased from Chemical Innovation Co., Ltd., (Bangkok, Thailand). Toluene was purchased from Union Petrochemical PCL (Bangkok, Thailand). Element14 PDMS 350 was purchased from Kendus Chem Co., Ltd., (Bangkok, Thailand). All materials were used as received without further purification.

**Synthesis of Oligolactide diols (OL-OHs):** OL-OHs were produced by ring opening reaction of L-lactide with HD. The concentrations of HD were 10, 20 and 30 mol% based on L-lactide content. The L-lactide and HD were added into a 250 mL three-neck round-bottom flask equipped with a thermometer and a magnetic stirrer. The temperature was raised to 140°C. When all materials were

melted and mixed homogeneously, stannous octoate (0.02 mol% of L-lactide) was added into the mixture. The temperature of the mixture was then raised to 160°C and maintained for 3 h. The samples were labelled with the mol% of HD in each preparation. For example, an oligolactide diol produced from 30 mol% of HD is designated as OLHD-OH-30.

**Synthesis of an Oligolactide Acrylate (OL-A):** Owing to its appropriate viscosity, OLHD-OH-30 was selected for functionalizing with AA. OLHD-OH-30 and the double stoichiometric amount of AA were added into a 250 mL three-neck round-bottom flask equipped with a thermometer, a magnetic stirrer, a N<sub>2</sub> gas inlet tube, a Dean-Stark separator and a reflux condenser. The stoichiometric amount of AA was calculated from the theoretical molecular weight of the OLHD-OH-30 and that of HD. Subsequently, p-TSA (1% w/w), DBHQ (0.1% w/w) and toluene (35% w/w) were added into the flask. The temperature of the mixture was then raised to 130°C. The N<sub>2</sub> gas was continuously sparged under the surface of the mixture for the entire reaction. After 16 h, the OL-A was purified by distillation under reduced pressure at 140°C for 1 h.

**Characterization:** The functional groups and structures of the OL-OHs and the OL-A were characterized by Fourier Transform Infrared Spectroscopy (FTIR) on a Perkin Elmer Spectrum 100 spectrometer. The chemical structures of the oligomers were determined by proton Nuclear Magnetic Resonance spectroscopy (<sup>1</sup>H-NMR) on a Bruker AVANCE III HD NMR spectrometer at 400 MHz using CDCl<sub>3</sub> as a solvent. Viscosities of the oligomers were measured by Brookfield Cone and Plate Viscometer High Shear CAP-2000+. The number-average molecular weights of OL-OHs were calculated from <sup>1</sup>H-NMR. The molecular weights of OL-OHs were also determined by Gel Permeation Chromatography (GPC) on a Shimadzu GPC 10A system with chloroform as a solvent and an injection rate of 1 mL min<sup>-1</sup> at 30°C.

**Preparation of UV-curable screen printing inks:** To evaluate the potential use of the OL-A in UV-curable application, a UV-curable screen printing ink was prepared. The OL-A (70% w/w) was mixed with HDDA (24% w/w), IHT-PI 1173 (5% w/w) and Element14 PDMS 350 (1% w/w) by a high-speed stirrer at a speed of 1,000 rpm for 10 min. The ink was printed through a 180 lines/cm screen printing mesh on flame-treated Polyethylene (PE), Polypropylene (PP) and PLA as well as untreated PLA sheets. Wet film thickness was 10 μ. The ink was cured at 25°C under a UV dryer having a

3 kW medium-pressure mercury lamp at a belt speed of 20 m min<sup>-1</sup>. The integral UV intensity was 400 mJ cm<sup>-2</sup>. The adhesion of the printed samples was determined according to ISO 2409:2013 Cross-cut test. A screen printing ink produced from Sartomer CN736, a commercial polyester acrylate was also formulated and tested as a comparison.

## RESULTS AND DISCUSSION

**Structure of Oligolactide diols (OL-OHs):** Oligolactide diols were produced by ring opening reaction of L-lactide with different amounts of the 1,6-hexanediol ring opener. The possible reaction scheme and its product are shown in Fig. 1. The FTIR spectra of OL-OHs are shown in Fig. 1. The small peaks at 2991, 2942 and 2863 cm<sup>-1</sup> were related to C-H stretching.

The peaks at 1380 and 1361 cm<sup>-1</sup> corresponded to C-H bending. Two peaks at 865 and 749 cm<sup>-1</sup> were attributed to C-C stretching. The C-O-C stretching peaks were observed at 1187, 1126, 1085 and 1044 cm<sup>-1</sup>. The strong peak at 1740 cm<sup>-1</sup> and the weak peak at 1266 cm<sup>-1</sup> were related to the C = O and C-O stretching of ester groups, respectively. The peak of -CH<sub>3</sub> bending was found at 1444 cm<sup>-1</sup>. These peaks indicated the aliphatic ester structure of the lactide oligomer (Vasafi *et al.*, 2012; Nikolic *et al.*, 2010). The -OH stretching peak was observed at 3522 cm<sup>-1</sup>, illustrating the presence of hydroxyl groups in the structure of OL-OHs. Moreover, the -CH bending of lactide monomer at 934 cm<sup>-1</sup> was not found in all samples, indicating that the lactide ring was already opened (Fang *et al.*, 2009). FTIR results reveal that the synthesized OL-OHs had a hydroxyl containing aliphatic ester structure.

The <sup>1</sup>H-NMR spectra of OL-OHs are shown in Fig. 3. The strong peak at 5.16 ppm (a) and the weak peak at 4.32 ppm (a') represented methine protons of the lactide unit in the repeating unit and at the chain end next to the hydroxyl group, respectively. The peaks at 1.56 ppm (b) and 1.38 ppm (b') were related to methyl

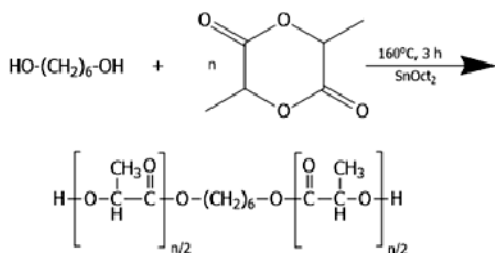


Fig. 1: Ring opening reaction scheme of L-lactide with 1,6-hexanediol

protons in the repeating unit and at the end of the OL-OH chains, respectively. The peaks at 4.12 ppm (c) and 1.45 ppm (d, e) were attributed to the outer and inner methylene protons of HD, respectively. The peak at 2.88 ppm (f) was related to the protons of the terminal hydroxyl groups (Vasafi *et al.*, 2012; Korhonen *et al.*, 2001). In addition, the FTIR and <sup>1</sup>H-NMR results showed that OLHD-OH-30 had higher hydroxyl content than the others. The reason was that it had the shortest lactide chain length due to the highest HD amount used in the ring opening reaction. The FTIR and <sup>1</sup>H-NMR results are in good agreement with the structure of the OL-OH

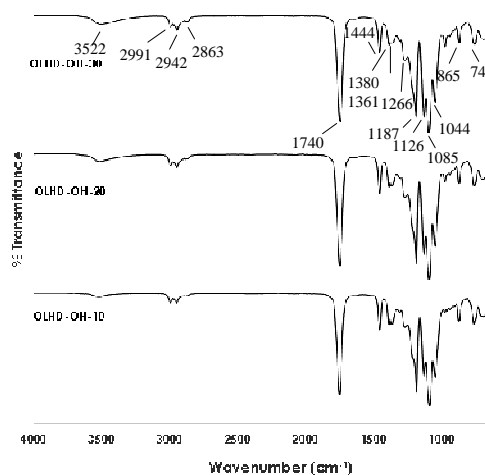


Fig. 2: FTIR spectra of OL-OHs

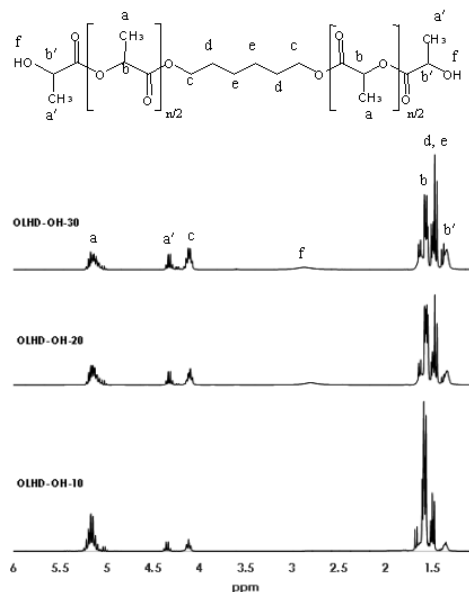


Fig. 3: <sup>1</sup>H-NMR spectra of OL-OHs

Table 1: Molecular weight, polydispersity index and viscosity of OL-OHs

Samples	M <sub>n</sub> : Theoretical/ g mol <sup>-1</sup>	M <sub>n</sub> : NMR/ g mol <sup>-1</sup>	M <sub>n</sub> : GPC/ g mol <sup>-1</sup>	M <sub>w</sub> : GPC/ g mol <sup>-1</sup>	PDI	Viscosity/CP
OLHD-OH-10	1,558	1,468	2,250	2,853	1.27	N/A
OLHD-OH-20	838	847	1,157	1,446	1.25	4,927
OLHD-OH-30	598	650	826	1,006	1.22	144

presented in Fig. 1. Therefore, it can be concluded that hydroxyl-terminated OL-OHs were successfully synthesized.

**Molecular weights of Oligolactide diols (OL-OHs):** From <sup>1</sup>H-NMR spectra, the number-average molecular weights (M<sub>n</sub>) of the OL-OHs could be calculated using Eq. 1:

$$M_n = \left( 144 \times \frac{I_{5.16} + I_{4.32}}{I_{4.32}} \right) + 118 \quad (1)$$

where, I<sub>5.16</sub> and I<sub>4.32</sub> are the integral intensities of the peaks at 5.16 ppm (a) and 4.32 ppm (a'), respectively (Vasafi *et al.*, 2012).

The M<sub>n</sub> values calculated according to Eq. 1 are illustrated in Table 1. The M<sub>n</sub> values ranged from 650-1468 g mol<sup>-1</sup> which were close to the theoretical values.

The molecular weights of OL-OHs determined by GPC are also presented in Table 1. The PDI of all OL-OHs was narrow approximately about 1.2 which was the characteristic of ring opening reaction. It can be observed that M<sub>n</sub> of OL-OHs decreased when the amount of HD increased. This observation was also reported by other researchers (Vasafi *et al.*, 2012; Liu *et al.*, 2013). It should be noted that the M<sub>n</sub> values from GPC were significantly higher than the theoretical M<sub>n</sub> values. This was due to the difficulty in the calibration for GPC at low molecular weights (Vasafi *et al.*, 2012).

Table 1 also shows the viscosities of OLHD-OH-20 and OLHD-OH-30. The viscosity of OLHD-OH-10 could not be measured because it was too viscous at room temperature. It can be observed that the viscosity of OL-OH decreased with the increasing amount of HD due to its lower molecular weight.

**Structure of an Oligolactide Acrylate (OL-A):** An oligolactide acrylate was synthesized by functionalizing OLHD-OH-30 with AA. The proposed reaction scheme of the acrylation and its product are shown in Fig. 4.

The FTIR spectrum of the OL-A is displayed in Fig. 5. The peaks at 1637 and 1620 cm<sup>-1</sup> were related to the C=C stretching of acrylate groups. The =CH<sub>2</sub> bending, wagging and twisting of acrylate groups were found at 1408, 984 and 810 cm<sup>-1</sup>, respectively. Additionally, the peak at 3522 cm<sup>-1</sup> belonging to the hydroxyl groups of the

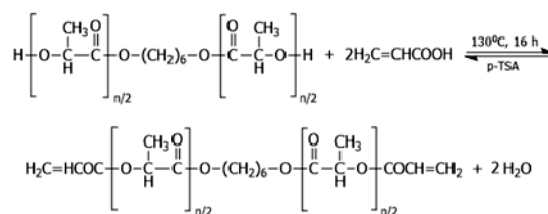


Fig. 4: Acrylation of an OL-OH with acrylic acid

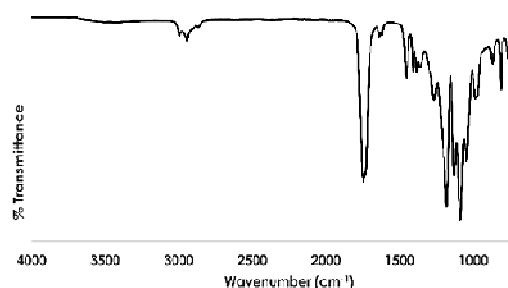


Fig. 5: FTIR spectrum of the OL-A

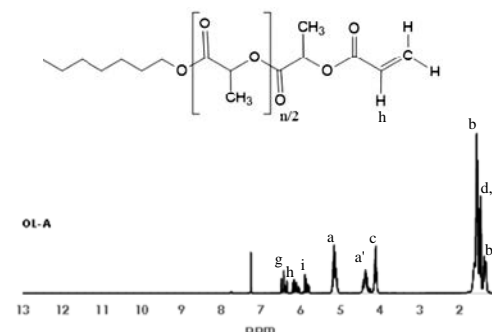


Fig. 6: <sup>1</sup>H-NMR spectrum of the OL-A

OL-OH disappeared, indicating that the hydroxyl groups completely reacted with the carboxyl groups of AA (Brokken *et al.*, 2011).

The <sup>1</sup>H-NMR spectrum of the OL-A is shown in Fig. 6. The peaks at 6.42 ppm (g), 6.13 ppm (h) and 5.81 ppm (i) were the characteristic peaks of protons of the acrylate double bond (Brown *et al.*, 2012). The broad peak at 2.88 ppm belonging to the protons of the terminal hydroxyl groups of the OL-OH was not observed. Moreover, the peak of the proton of the carboxyl group of AA at 12 ppm (j) as shown in Fig. 7 was not found in the

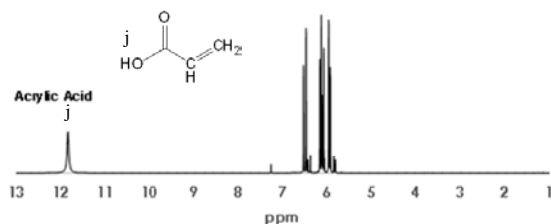


Fig. 7: <sup>1</sup>H-NMR spectrum of acrylic acid

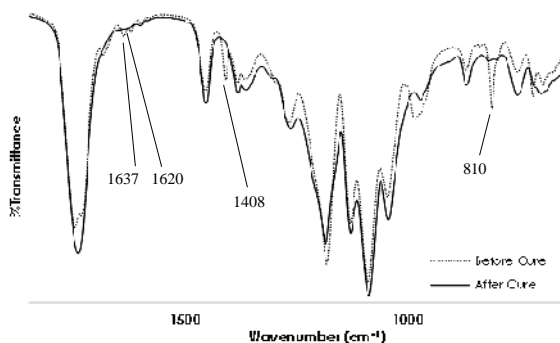


Fig. 8: FTIR spectra of the UV-curable screen printing inks before and after cure

spectrum of the OL-A. The <sup>1</sup>H-NMR result was in accordance with the FTIR result suggesting that the functionalization of the OL-OH with AA was successful.

**Screen printing inks:** The FTIR spectra of a UV-curable screen printing ink containing the OL-A is displayed in Fig. 8. The C=C stretching peaks at 1637 and 1620 cm<sup>-1</sup> and the =CH<sub>2</sub> bending peaks at 1408 and 810 cm<sup>-1</sup> which were related to the acrylate end group were disappeared after UV curing. This confirmed that the ink was undergone photo-initiated free radical polymerization and transformed the state of ink from liquid to solid film.

The adhesion of the ink was evaluated based on ISO 2409:2013. It was found that the printing ink containing the OL-A had adhesion on treated PLA and treated PE at level 0 (excellent adhesion) while it showed unsatisfactory results at level 4 (poor adhesion) and at level 5 (no adhesion) on untreated PLA and treated PP, respectively. A printing ink formulated from a commercial polyester acrylate (Sartomer CN736) had similar adhesion on each substrate as did that containing the obtained OL-A. These results showed that it is possible to use OL-As as an oligomer for UV-curable screen printing inks. Nevertheless, further studies on the synthesis of OL-As and formulation of the screen printing inks should be carried out in order to expand the use of OL-As in screen printing application.

## CONCLUSION

Hydroxyl-terminated oligolactide diols were successfully synthesized by ring opening reaction of L-lactide with 1,6-hexanediol. The molecular weight and viscosity of the prepared oligolactide diols can be modified by varying the amount of diols used in ring opening reaction. Furthermore, an oligolactide acrylate was successfully synthesized by functionalizing an oligolactide diol with acrylic acid and it can be used in the formulation of a UV-curable screen printing ink. The ink film can adhere well on treated polylactide and treated polyethylene. This proves that the oligolactide acrylate can be potentially used in UV-curable application.

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## REFERENCES

- Brokken, Z.J.C.M., V.O.L.J. Asselen, W.E. Kleinjan and V.D.R. Belt, 2011. Photocatalysed (meth) acrylate polymerization by (antimony-doped) tin oxide nanoparticles and photoconduction of their crosslinked polymer nanoparticle composites. *J. Nanotechnol.*, 2010: 1-16.
- Brown, W.H., C.S. Foote and B.L. Iverson, E.V. Anslyn, 2012. *Organic Chemistry*. Cengage Learning, Boston, Massachusetts, ISBN:978-0-8400-5498-2, Pages: 1161.
- Chang, C.W. and K.T. Lu, 2013. Linseed-oil-based waterborne UV/air dual-cured wood coatings. *Prog. Organic Coat.*, 76: 1024-1031.
- Fang, L., R. Qi, L. Liu, G. Juan and S. Huang, 2009. Synthesis of poly (L-lactide) via solvothermal method. *Int. J. Polym. Sci.*, 2009: 1-7.
- Habib, F. and M. Bajpai, 2011. Synthesis and characterization of acrylated epoxidized soybean oil for UV cured coatings. *Chem. Chem. Technol.*, 5: 317-326.
- Helminen, A., H. Korhonen and J.V. Seppala, 2001. Biodegradable crosslinked polymers based on triethoxysilane terminated polylactide oligomers. *Polym.*, 42: 3345-3353.
- Helminen, A.O., H. Korhonen, and J.V. Seppala, 2002. Structure modification and crosslinking of methacrylated polylactide oligomers. *J. Appl. Polym. Sci.*, 86: 3616-3624.
- Hiltunen, K., J.V. Seppala and M. Harkonen, 1997. Effect of catalyst and polymerization conditions on the preparation of low molecular weight lactic acid polymers. *Macromolecules*, 30: 373-379.

- Korhonen, H., A. Helminen and J.V. Seppala, 2001. Synthesis of polylactides in the presence of co-initiators with different numbers of hydroxyl groups. *Polymer*, 42: 7541-7549.
- Kulkarni, R.D., M.E. Chaudhari and S. Mishra, 2013. UV cure acrylate monomers: synthesis, analysis and storage. *Pigment Resin Technol.*, 42: 53-67.
- Liu, J., C. Peizhen, H. Jiang and L. Chen, 2013. Synthesis and chain extension of hydroxyl terminated poly (lactic acid) oligomers and application in the blends. *Polym. Compos.*, 34: 305-312.
- Nikolic, L., I. Ristic, B. Adnadjevic, V. Nikolic, J. Jovanovic and M. Stankovic, 2010. Novel microwave-assisted synthesis of poly D, L-lactide: The influence of monomer initiator molar ratio on the product properties. *Sensors*, 10: 5063-5073.
- Rengasamy, S. and V. Mannari, 2013. Development of soy-based UV-curable acrylate oligomers and study of their film properties. *Prog. Organic Coat.*, 76: 78-85.
- Sin, L.T., A.R. Rahmat and W.A. Rahman, 2012. *Polylactic Acid: PLA Biopolymer Technology and Applications*. William Andrew, Amsterdam, Netherlands, ISBN:978-1-4377-4459-0, Pages: 340.
- Tounthai, J., A. Petchsuk, P. Opaprakasit and M. Opaprakasit, 2013. Curable polyester precursors from polylactic acid glycolyzed products. *Polym. Bull.*, 70: 2223-2238.
- Vasafi, I.H., M. Sadeghi, G. Mir and H. Garmabi, 2012. Synthesis of hydroxyl terminated poly (lactic acid) via polycondensation: An equation to predict molecular weight based on the reaction parameters. *J. Appl. Polym. Sci.*, 125: 604-615.
- Wicks, Z.W., F.N. Jones and S.P. Pappas, 1999. *Organic Coating: Science and Technology*. 2nd Edn., John Wiley & Sons, New York, USA.