

REFERENCES

1. Wang, C. H., H. Li., and X. Zhao. "Ring opening polymerization of L-lactide initiated by creatinine." *Biomaterials* 25, 27 (2004): 5797-801.
2. Bendix, D. "Chemical synthesis of polylactide and its copolymer for medical applications." *Polymer Degradation and Stability* 59, 1-3 (1998): 129-35.
3. Channuan, W., et al. "The structure of crystallisable copolymers of L-lactide, epsilon-caprolactone and glycolide." *Polymer* 46, 17 (2005): 6411-28.
4. Jung, S. W., et al. "Drug release from core-shell type nanoparticles of poly(DL-lactide-co-glycolide)-grafted dextran." *Journal of Microencapsulation* 22, 8 (2005): 901-11.
5. Dutkeiwicz, S., D. Grochowska-Lapienis, and W. Tomaszewski. "Synthesis of poly(L+) lactic acid) by polycondensation method in solution." *Fibres & Textiles in Eastern Europe* 11, 4 (2003): 66-70.
6. Kricheldorf, H. R., I. Kreiser-Saunders, and C. Boettcher. "Polylactones .31. Sn(II)Octoate-initiated Polymerization of L-lactide - A mechanistic study." *Polymer* 36, 6 (1995): 1253-59.
7. Kricheldorf, H. R., and S. R. Lee. "Polylactone .32. High-Molecular Weight Polylactides by Ring-Opening Polymerization with Dibutylmagnesium or Butylmagnesium Chloride." *Polymer* 36, 15 (1995): 2995-3003.
8. Kricheldorf, H. R., I. Kreiser-Saunders, and A. Stricker. "Polylactones .48. SnOct(2)-initiated polymerizations of lactide: A mechanistic study." *Macromolecules* 33, 3 (2002): 702-09.
9. Eguiburu, J. L., et al. "Ring-opening polymerization of L-lactide initiated by (2-methacryloxy) ethyloxy-aluminum trialkoxides. I. Kinetics." *Macromolecules* 32, 25 (1999): 8252-58.
10. Abe, A., Albertsson, A. C., Cantow, H. J., Dusek, K., Edwards, S., Hocker, H., Joanny, J. F., Kausch, H. H., Lee, K. S., McGrath, J. E., Monnerie, L., Stupp, S. I., Suter, U. W., Wenger, G., Young, R. J., "Advance in Polymer Science" *Springer-Verlag Berlin Heidelberg*. (2002): 16-18, 45-46, 48-49, 59-61, 115-116, 150-151.

11. Gattin, R., et al. "Biodegradation study of a starch and poly(lactic acid) co-extruded material in liquid, composting and inert mineral media." *International Biodeterioration & Biodegradation* 50, 1 (2002): 25-31.
12. Kasuga, T., et al. "Preparation and mechanical properties of polylactic acid composites containing hydroxyapatite fibers." *Biomaterials* 22, 1 (2001): 19-23.
13. Aida, T., Allcock, H. R., Brunelle, D. J., Chujo, Y., Crivello, J. V., Duda, A., Goethals, E. J., Inoue, S., Kim, J., Kobayashi, S., Kubisa, P., Penczek, S., Quirk, R. P., Seagusa, T., Schrock, R. R., and Slomkowski, S. "Ring-Opening Polymerization Mechanisms, Catalysis, Structure, Utility" *Hanser Publishers, Munich Vienna New York Barcelona*. (1993): 2-6, 17-15, 88.
14. Touminen, J., et al. "Biodegradation of lactic acid based polymers under controlled composting conditions and evaluation of the ecotoxicological impact." *Biomacromolecules* 3, 3 (2002): 445-55.
15. Yoo, D. K., D. Kim, and D. S. Lee. "Synthesis of lactide from oligomeric PLA: Effects of temperature, pressure, and catalyst." *Macromolecular Research* 14, 5 (2006): 510-16.
16. Yu, C. P., X. Li, and Z. Q. Shen. "Ring-opening homopolymerization of lactides." *Progress in Chemistry* 19, 1 (2007): 136-44.
17. Kiremitci-Gumusderelioglu, M. and G. Diniz. "Synthesis, characterization and in vitro degradation of poly(dl-lactide)/poly(dl-lactide-co-glycolide) films." *Turkish Journal of Chemistry* 23, 2 (1999): 153-61.
18. Touminen, J., J. Kylma, and J. Seppala. "Chain extending of lactic acid oligomers .2. Increase of molecular weight with 1,6-hexamethylene diisocyanate and 2,2'-bis(2-oxazoline)." *Polymer* 43, 1 (2002): 3-10.
19. Kylma, J., et al. "Chain extending of lactic acid oligomers. Effect of 2,2'-bis(2-oxazoline) on 1,6-hexamethylene diisocyanate linking reaction." *Polymer* 42, 8 (2001): 3333-43.
20. Tarvainen, T., et al. "Degradation of and drug release from a novel 2,2-bis(2-oxazoline) linked poly(lactic acid) polymer." *Journal of Controlled Release* 81, 3 (2002): 251-61.

21. Lewis, K. J., W. J. Irwin, and S. Akhtar. "Biodegradable Poly(L-lactic Acid) Matrices for the Sustained Delivery of Antisense Oligonucleotides." *Journal of Controlled Release* 37, 1-2 (1995): 173-83.
22. Mchta, R., et al. "Synthesis of poly(lactic acid): A review." *Journal of Macromolecular Science-Polymer Reviews* C45, 4 (2005): 325-49.
23. Korhonen, H., A. Helminen, and J. V. Seppala. "Synthesis of polylactides in the presence of co-initiators with different numbers of hydroxyl groups." *Polymer* 42, 18 (2001): 7541-49.
24. Kohn, R. D., et al. "Ring-opening polymerization of D,L-lactide with bis(trimethyl triazacyclohexane) praseodymium triflate." *Catalysis Communications* 4, 1 (2003): 33-37.
25. Kricheldorf, H. R. and C. Boettcher. "Polylactones .26. Lithium Alkoxide-Initiated Polymerizations of L-lactide." *Makromolekulare Chemie-Macromolecular Chemistry and Physics* 194, 6 (1993): 1665-69.
26. Kricheldorf, H. R. and D. O. Damrau. "Polylactones, 33-Polymerization of L-lactide catalyzed by zinc amino acid salts." *Macromolecular Chemistry and Physics* 199, 8 (1998): 1747-52.
27. Kricheldorf, H. R. and J. Mcicrhaack. "Polylactones .22. ABA Triblock Copolymers of L-lactide and Poly(Ethylene Glycol)." *Makromolekulare Chemie-Macromolecular Chemistry and Physics* 194, 2 (1993): 715-25.
28. Sarasua, J. R., et al. "Crystallization and melting behavior of polylactides." *Macromolecules* 31, 12 (1998): 3895-905.
29. Sun, J. Q., et al. "The ring-opening polymerization of D,L-lactide catalyzed by new complexes of Cu, Zn, Co, and Ni Schiff base derived from salicylidene and L-aspartic acid." *Journal of Applied Polymer Science* 86, 13 (2002): 3312-15.
30. Seppala, J. V., A. O. Helminen, and H. Korhonen. "Degradable polyesters through chain linking for packing and biomedical applications." *Macromolecular Bioscience* 4, 3 (2004): 208-17.
31. Touminen, J., and J. V. Seppala. "Synthesis and characterization of lactic acid based poly(ester-amide)." *Macromolecules* 33, 10 (2000): 3530-35.

32. Tsuji, H. and Y. Ikada. "Properties and morphology of poly(L-lactide) 4. Effects of structural parameters on long-term hydrolysis of poly(L-lactide) in phosphate-buffered solution." *Polymer Degradation and Stability* 67, 1 (2000): 179-89.
33. Yang, X. Q., et al. "Synthesis and properties of collagen/polylactic acid blends." *Journal of Applied Polymer Science* 94, 4 (2004): 1670-75.
34. Tarvainen, T., et al. "Drug release profiles from and degradation of a novel biodegradable polymer, 2,2-bis(2-oxazoline) linked poly(epsilon-caprolactone)." *European Journal of Pharmaceutical Sciences* 16, 4-5 (2002): 323-31.

APPENDICES

APPENDIX A

NMR spectra of L-lactide and poly(L-lactic acid)

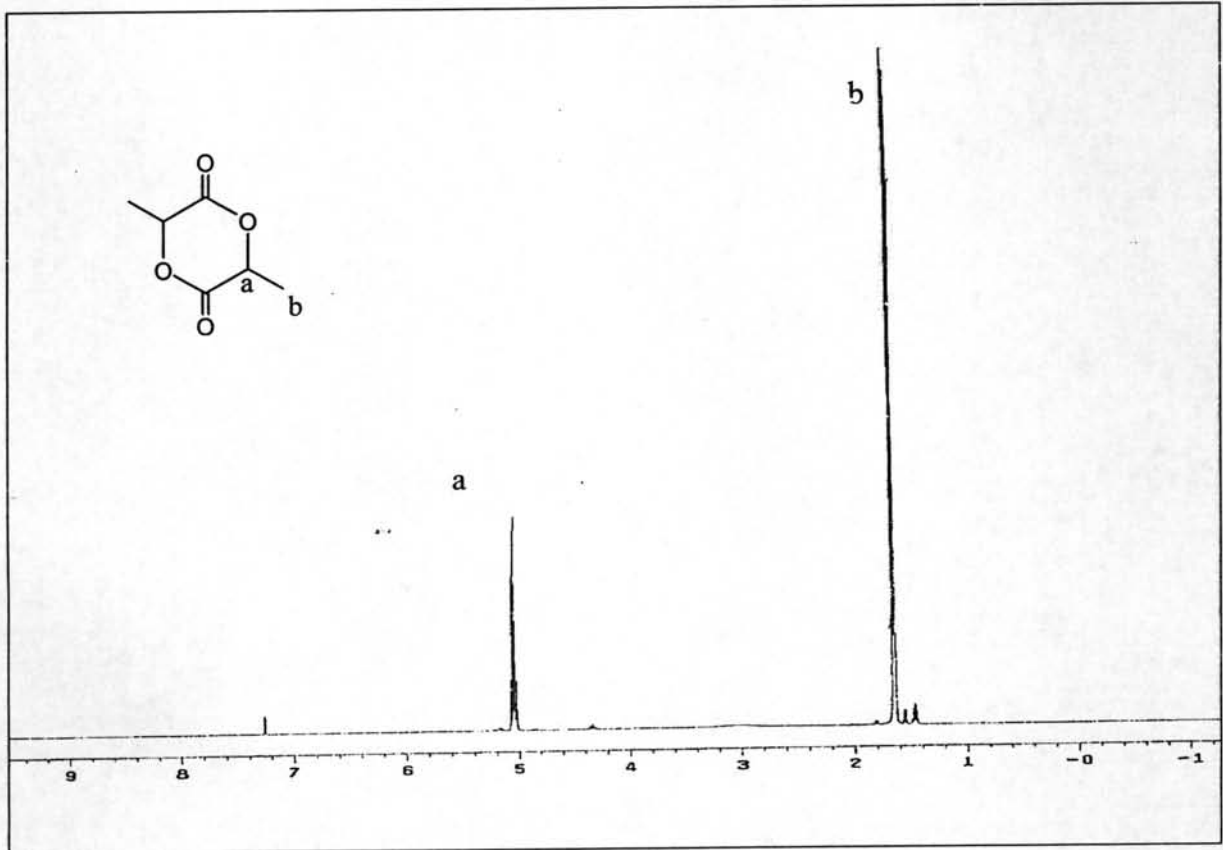


Figure A-1 400 MHz ^1H NMR spectrum of L-lactide

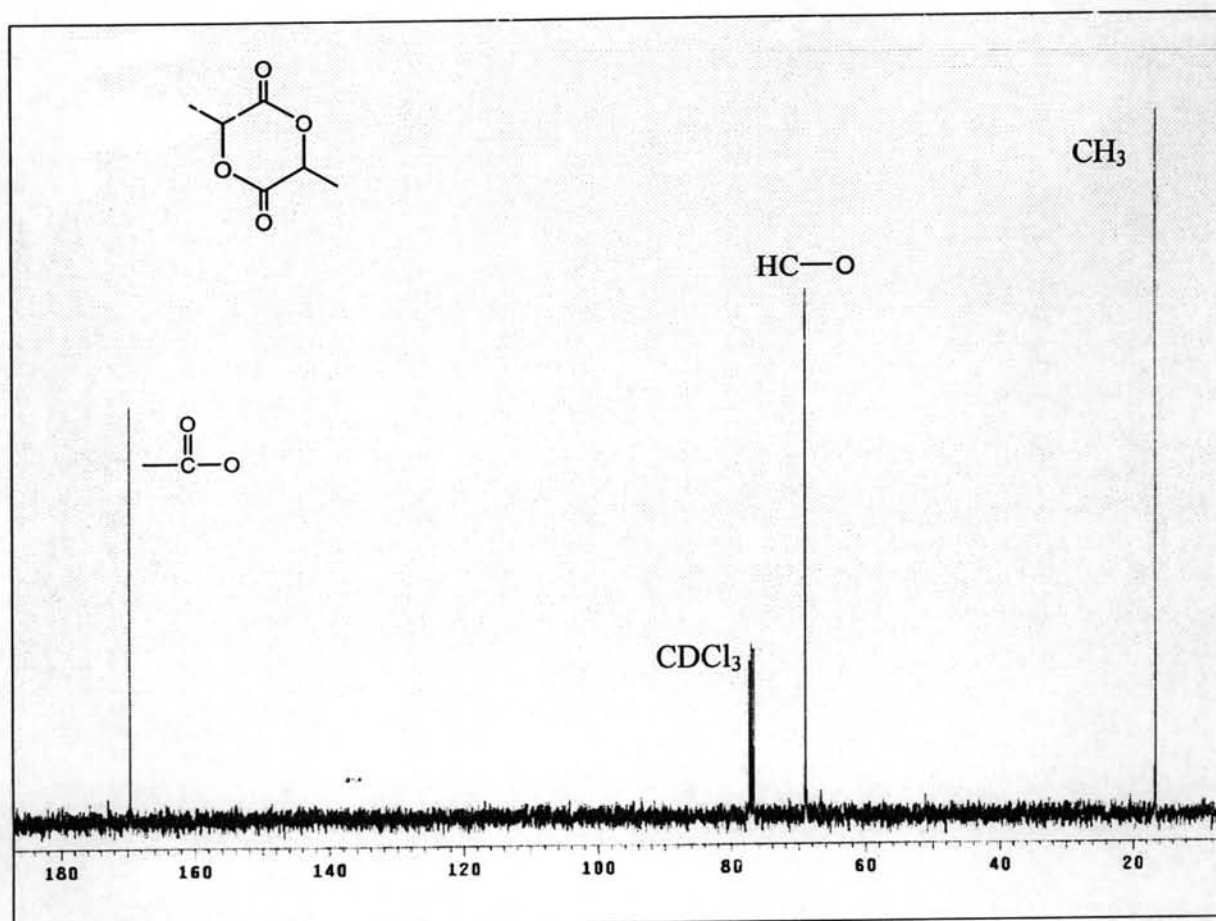


Figure A-2 400 MHz ^{13}C NMR spectrum of L-lactide

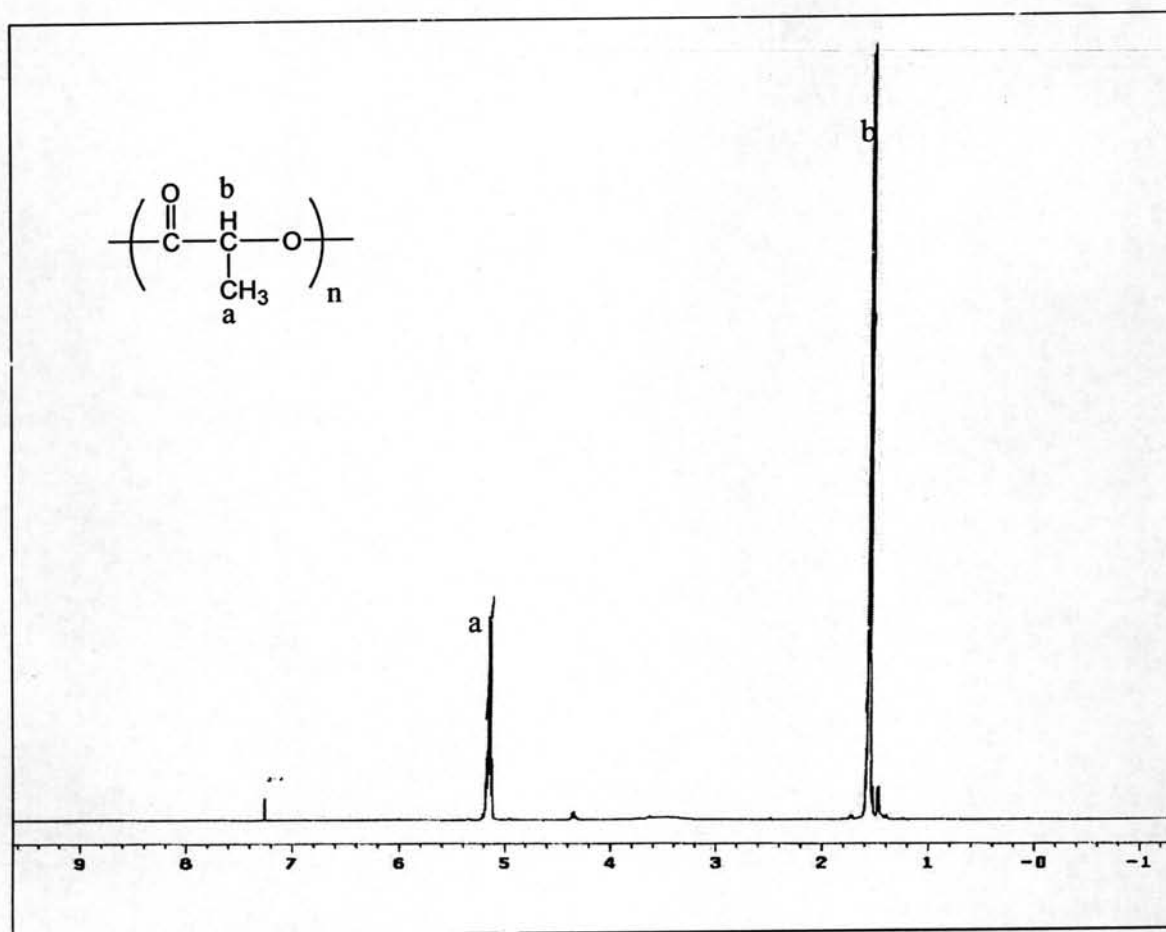


Figure A-3 400 MHz ^1H NMR spectrum of poly(L-lactic acid), 0.3 % w/w initiator

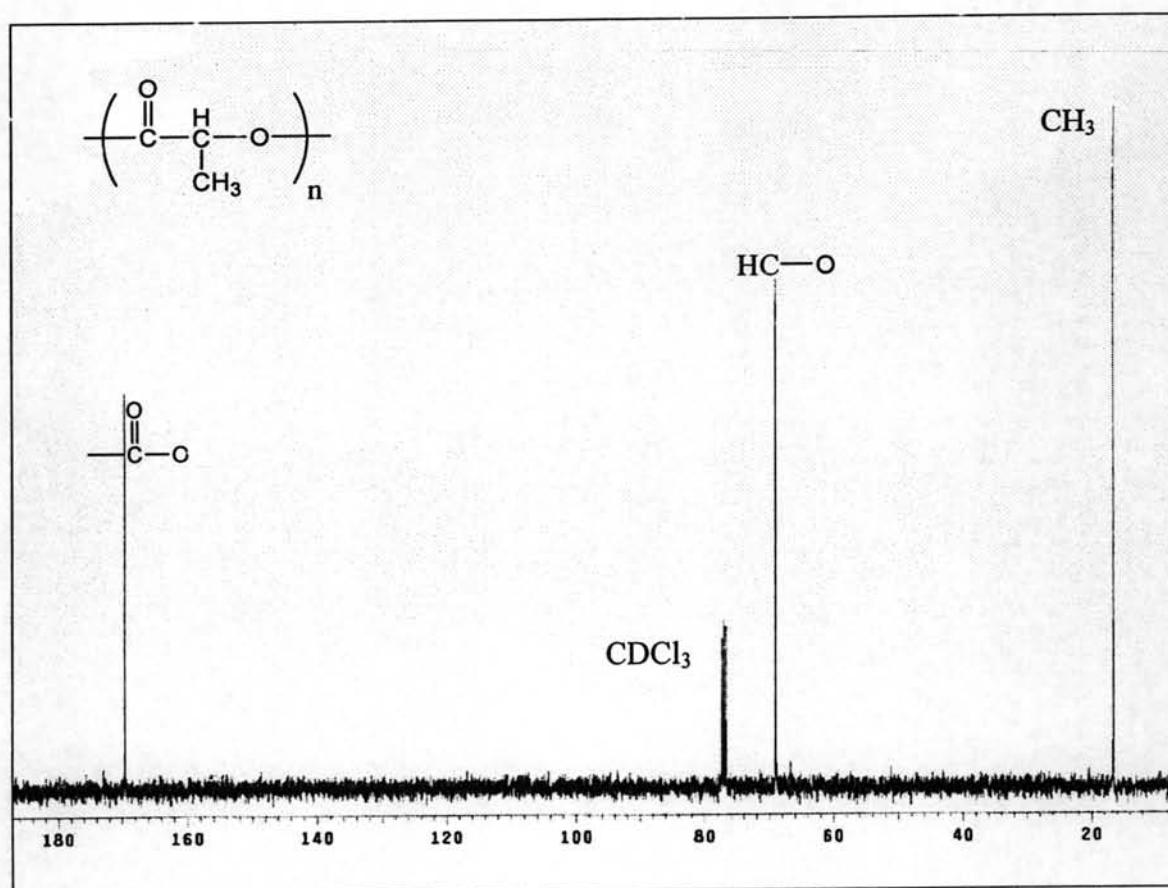


Figure A-4 400 MHz ^{13}C NMR spectrum of poly(L-lactic acid), 0.3 % w/w initiator

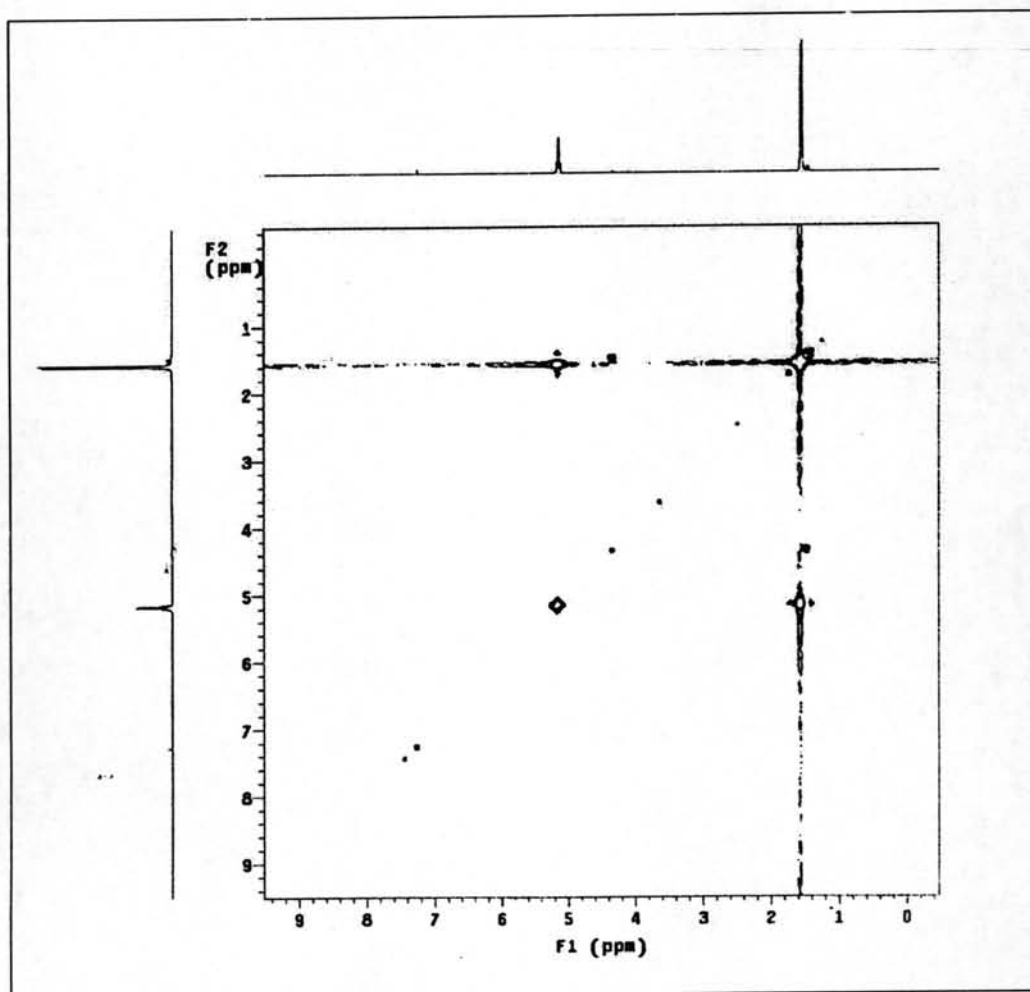


Figure A-5 400 MHz COSY-NMR spectrum of PLLA, 0.3 % w/w initiator

APPENDIX B

GPC chromatogram of poly(L-lactic acid)

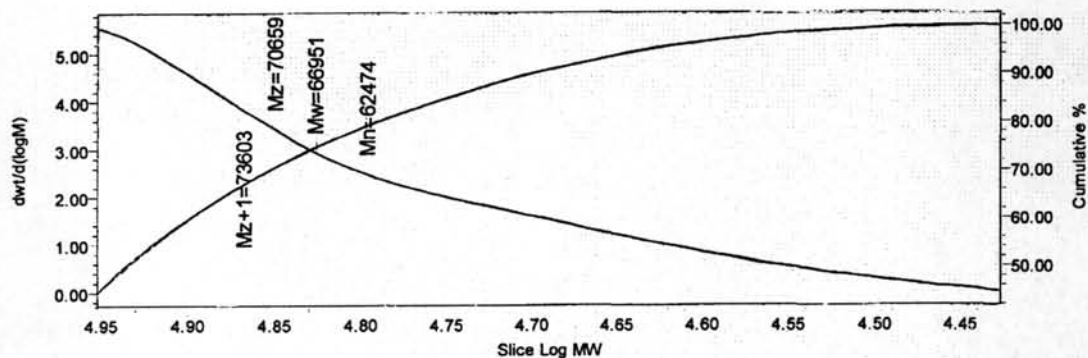


Figure B-1 GPC chromatogram of standard PLLA (commercial grade) from Taiwan

$$\overline{M}_w = 66951$$

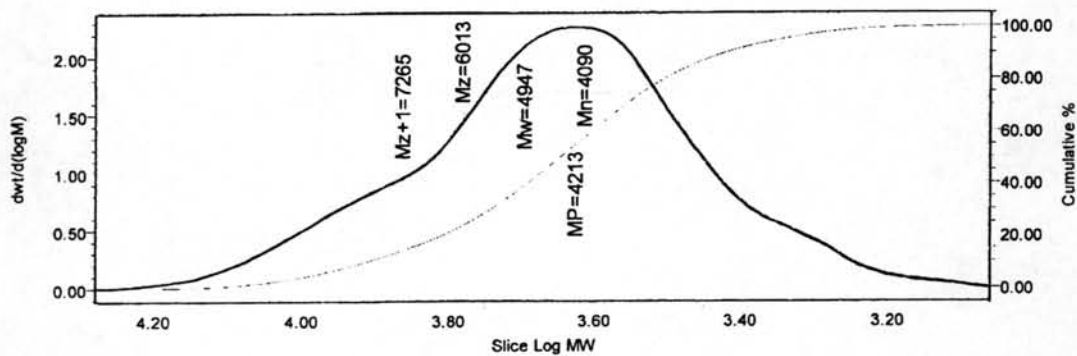


Figure B-2 GPC chromatogram of PLLA (at 120 °C, 12 hours) sample 1 in table 4.2

using $\text{Sn}(\text{Oct})_2$ as the initiator, $\overline{M}_w = 4947$

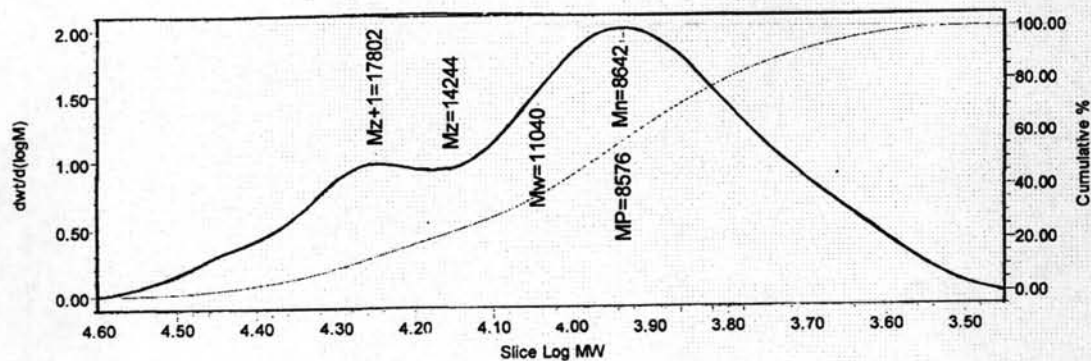


Figure B-3 GPC chromatogram of PLLA (at 120 °C, 24 hours) sample 2 in table 4.2 and sample 1 in table 4.5 using $\text{Sn}(\text{Oct})_2$ as the initiator, $\bar{M}_w = 11040$

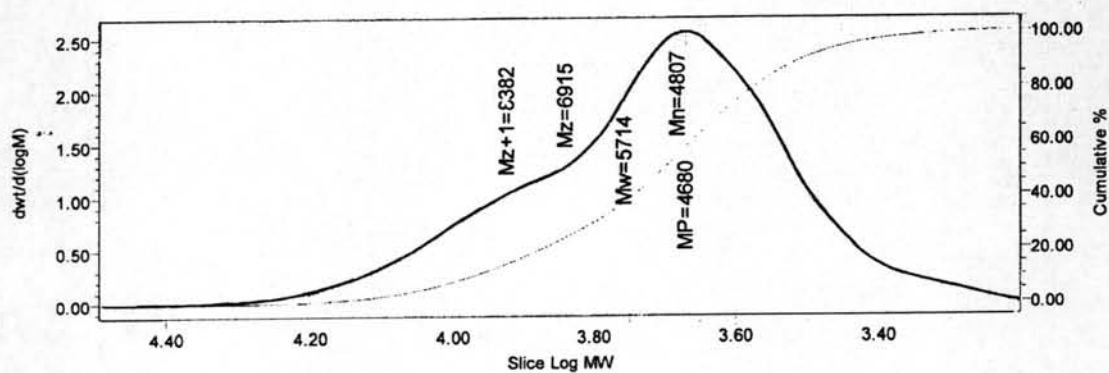


Figure B-4 GPC chromatogram of PLLA (at 120 °C, 12 hours) sample 2 in table 4.2 and sample 9 in table 4.6 using $\text{Sn}(\text{Oct})_2$ as the initiator, $\bar{M}_w = 5714$

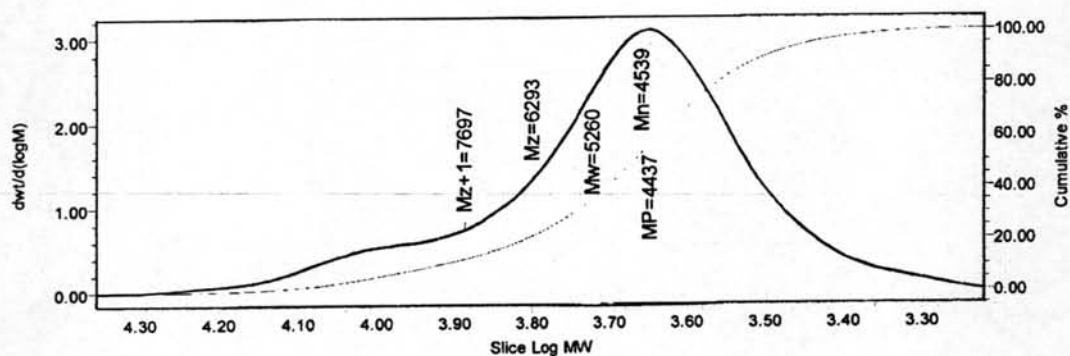


Figure B-5 GPC chromatogram of PLLA (at 100 °C, 96 hours) sample 1 in table 4.3 using creatine hydrate as the initiator, $\bar{M}_w = 5260$

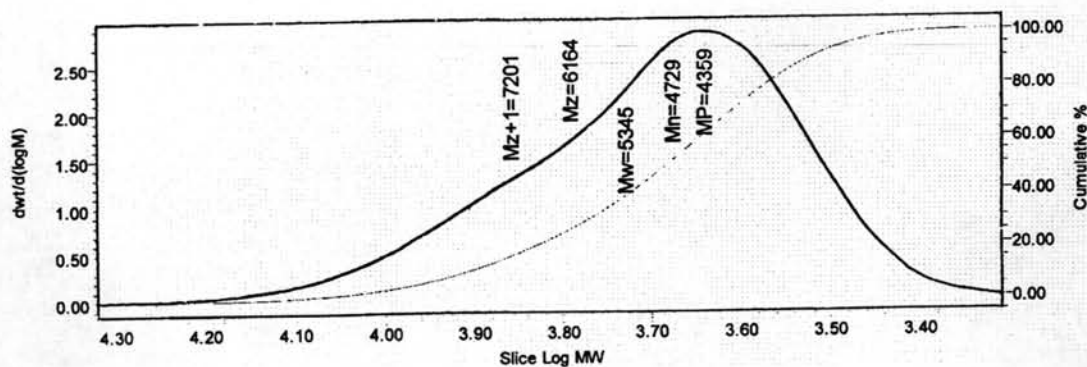


Figure B-6 GPC chromatogram of PLLA (at 120 °C, 96 hours) sample 2 in table 4.3 and sample 3 in table 4.4 using creatine hydrate as the initiator, $\overline{M}_w = 5345$

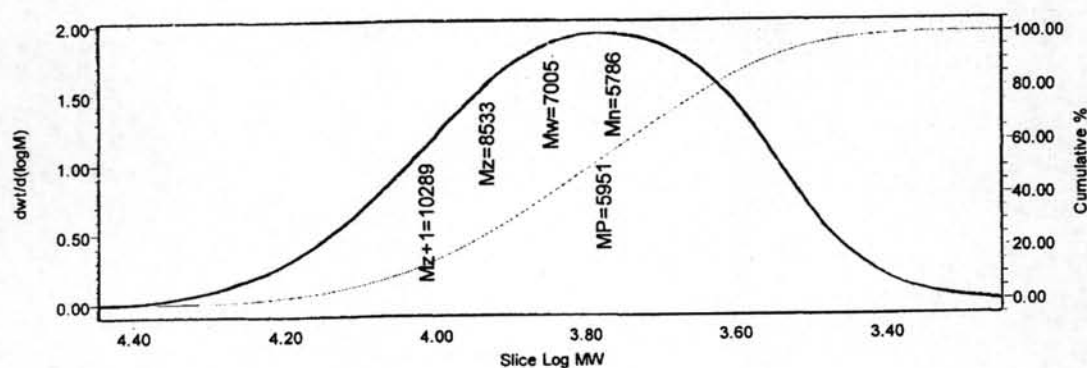


Figure B-7 GPC chromatogram of PLLA (at 140 °C, 96 hours) sample 3 in table 4.3 using creatine hydrate as the initiator, $\overline{M}_w = 7005$

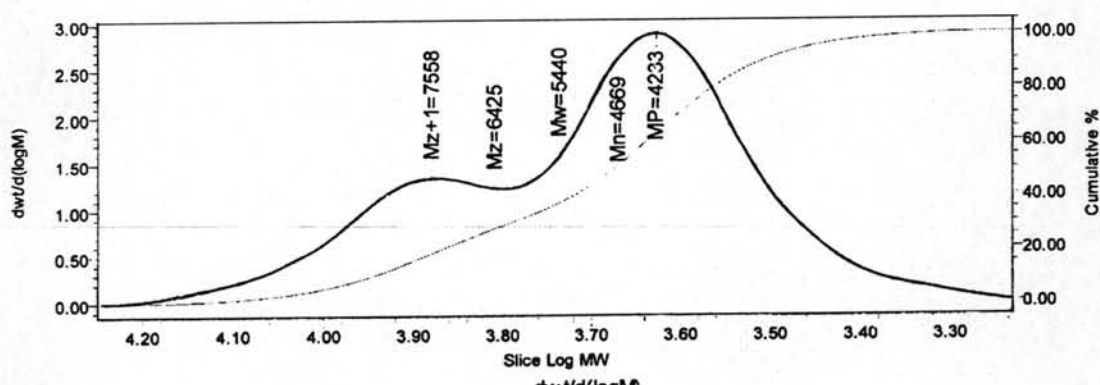


Figure B-8 GPC chromatogram of PLLA (at 120 °C, 24 hours) sample 1 in table 4.4, sample 4 in table 4.5 and sample 13 in table 4.6 using creatine hydrate as the initiator, $\overline{M}_w = 5440$

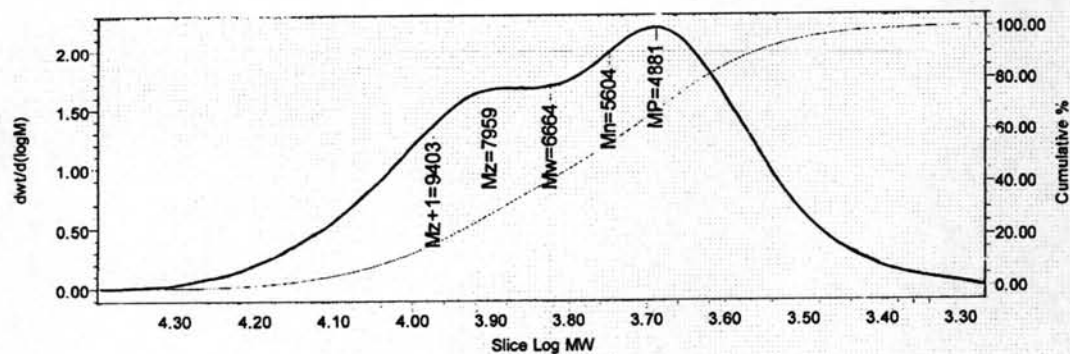


Figure B-9 GPC chromatogram of PLLA (at 120 °C, 48 hours) sample 2 in table 4.4, sample 7 in table 4.5 and sample 17 in table 4.6 using creatine hydrate as the initiator, $\overline{M}_w = 6664$

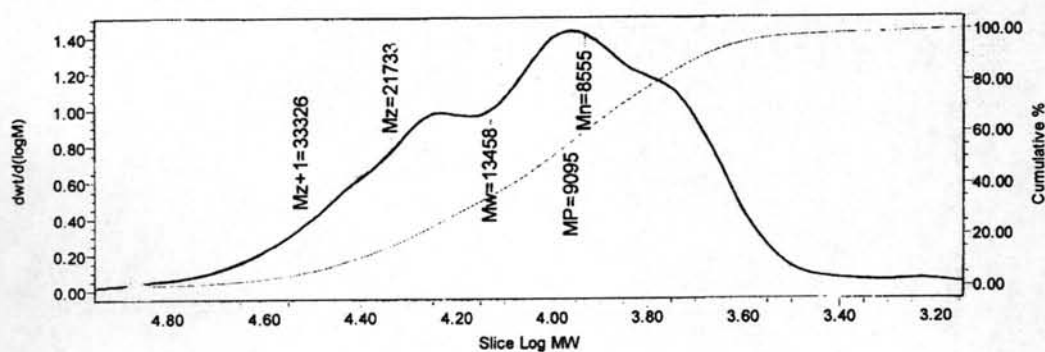


Figure B-10 GPC chromatogram of PLLA (at 120 °C, 24 hours) sample 2 in table 4.5 using HMDI as chain extender at the ratio of 1:1.1, $\overline{M}_w = 13458$

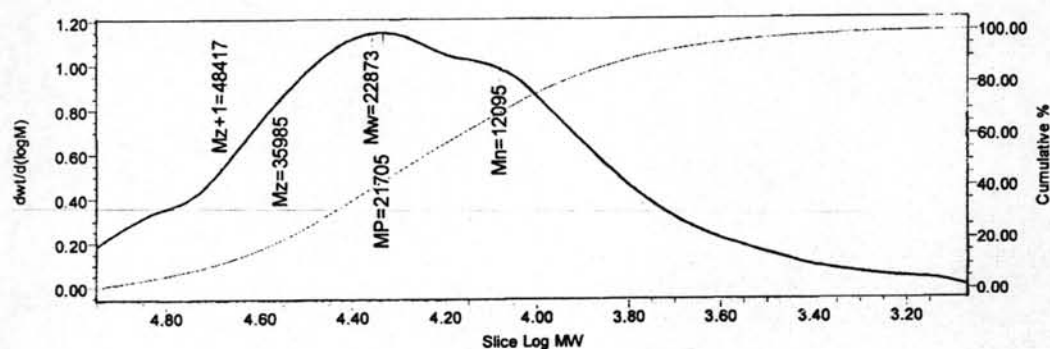


Figure B-11 GPC chromatogram of PLLA (at 120 °C, 24 hours) sample 3 in table 4.5 using tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer as chain extender at the ratio of 1:1.1, $\overline{M}_w = 22873$

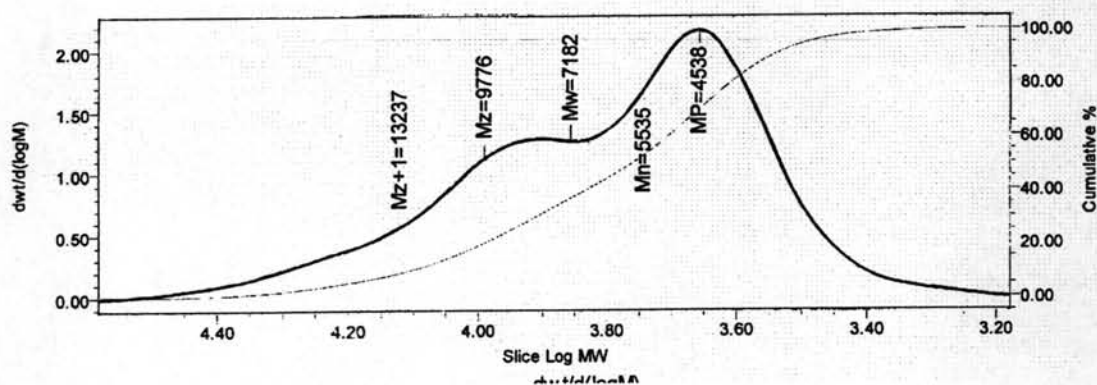


Figure B-12 GPC chromatogram of PLLA (at 120 °C, 24 hours) sample 5 in table 4.5 using HMDI as chain extender at the ratio of 1:1.1, $\overline{M}_w = 7182$

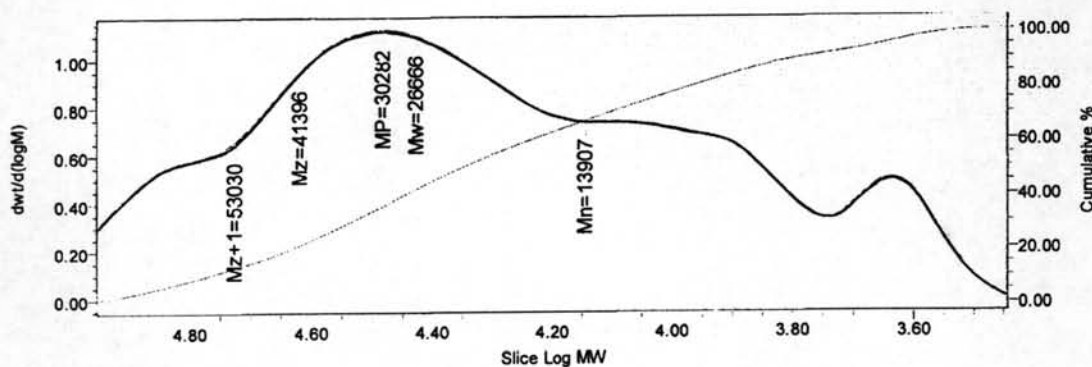


Figure B-13 GPC chromatogram of PLLA (at 120 °C, 24 hours) sample 6 in table 4.5 using tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer as chain extender at the ratio of 1:1.1, $\overline{M}_w = 26666$

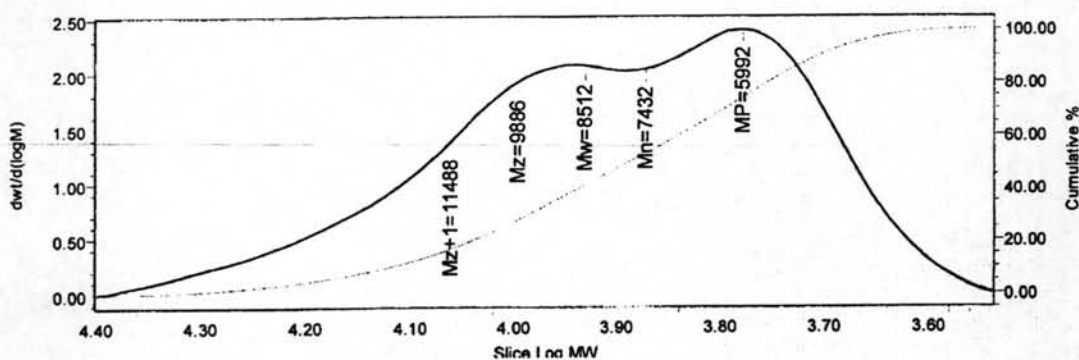


Figure B-14 GPC chromatogram of PLLA (at 120 °C, 48 hours) sample 8 in table 4.5 using HMDI as chain extender at the ratio of 1:1.1, $\overline{M}_w = 8512$

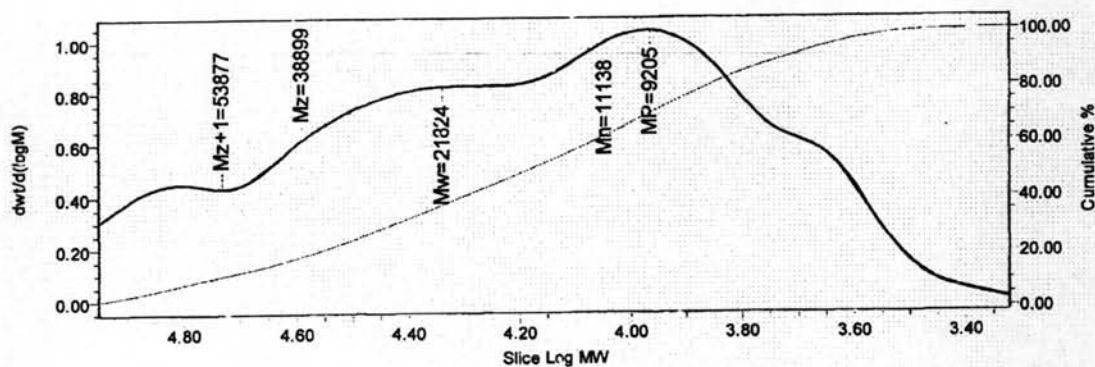


Figure B-15 GPC chromatogram of PLLA (at 120 °C, 48 hours) sample 9 in table 4.5 using tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer as chain extender at the ratio of 1:1.1, $\overline{M}_w = 21824$

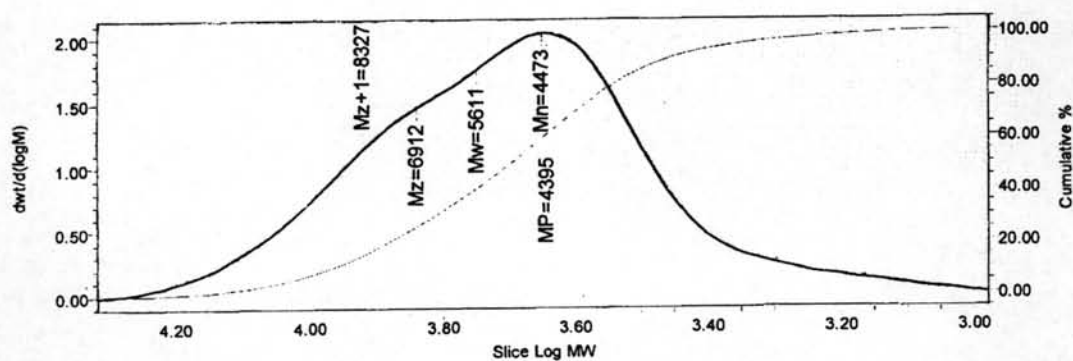


Figure B-16 GPC chromatogram of PLLA (at 120 °C, 24 hours) sample 1 in table 4.6 without chain extender, $\overline{M}_w = 5611$

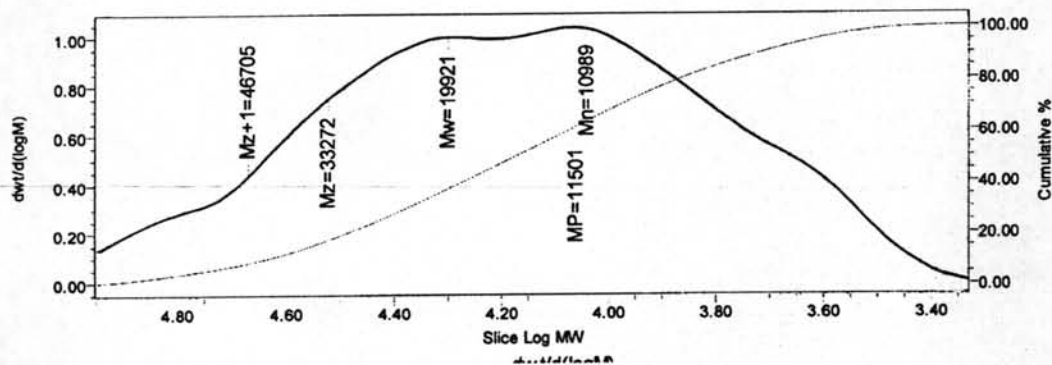


Figure B-17 GPC chromatogram of sample 2 in table 4.6: PLLA (at 120 °C, 24 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:0.5, $\overline{M}_w = 19921$

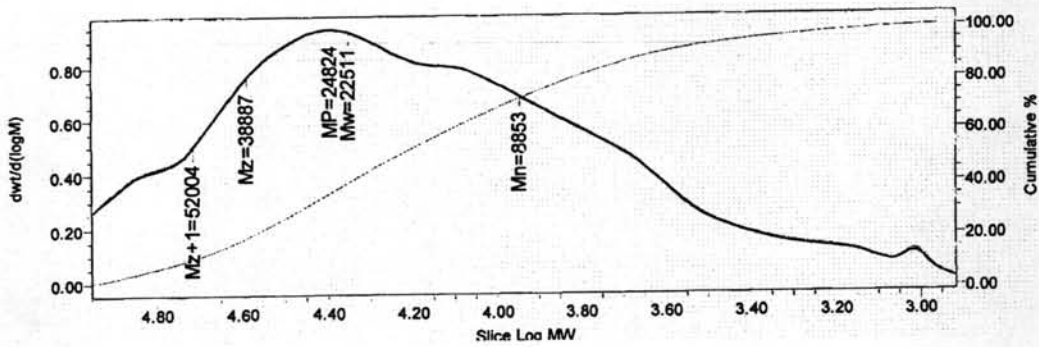


Figure B-18 GPC chromatogram of sample 3 in table 4.6: PLLA (at 120 °C, 24 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:1.1, $\overline{M}_w = 22511$

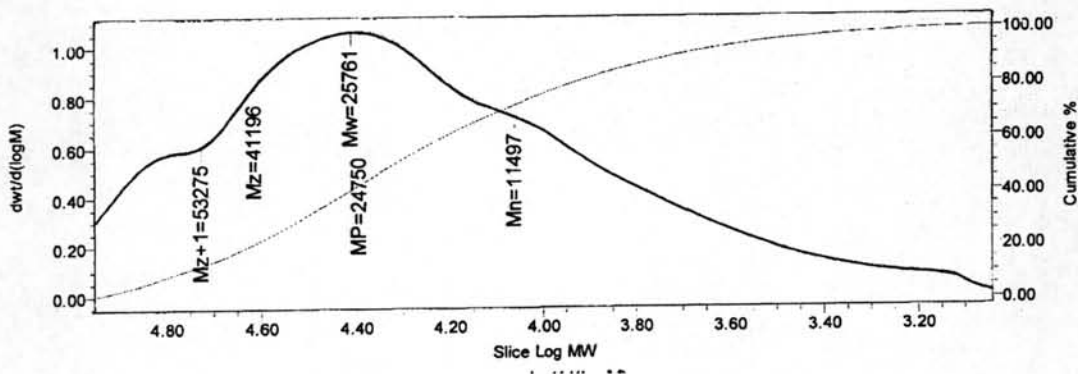


Figure B-19 GPC chromatogram of sample 4 in table 4.6: PLLA (at 120 °C, 24 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:2, $\overline{M}_w = 25761$

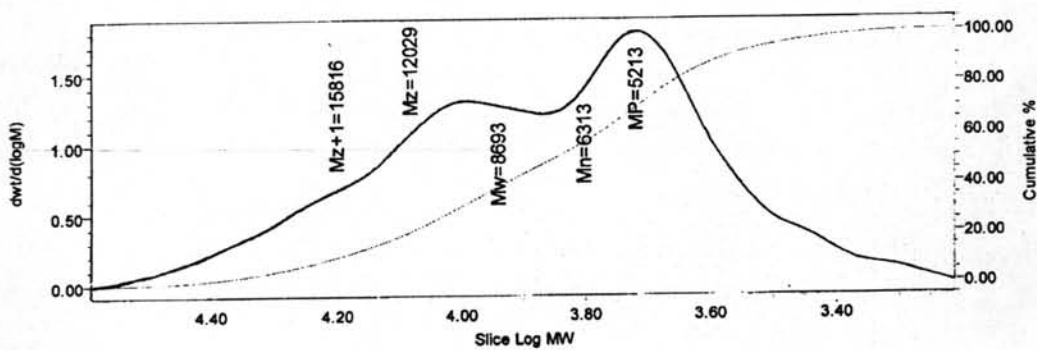


Figure B-20 GPC chromatogram of sample 5 in table 4.6: PLLA (at 120 °C, 24 hours) without chain extender, $\overline{M}_w = 8693$

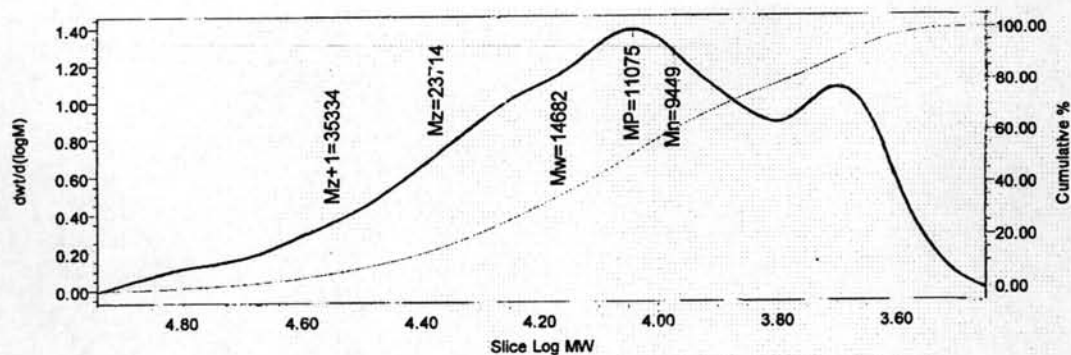


Figure B-21 GPC chromatogram of sample 6 in table 4.6: PLLA (at 120°C, 24 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:0.5, $\overline{M}_w = 14682$

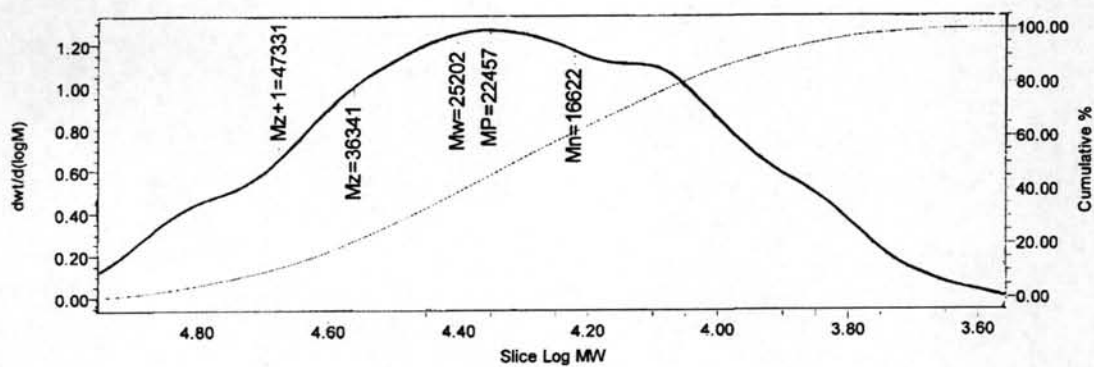


Figure B-22 GPC chromatogram of sample 7 in table 4.6: PLLA (at 120°C, 24 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:1.1, $\overline{M}_w = 25202$

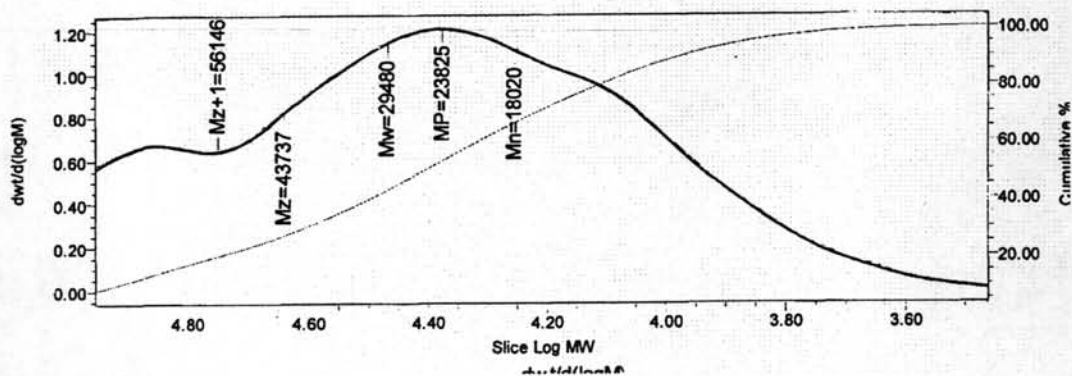


Figure B-23 GPC chromatogram of sample 8 in table 4.6: PLLA (at 120 °C, 24 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:2, $\overline{M}_w = 29480$

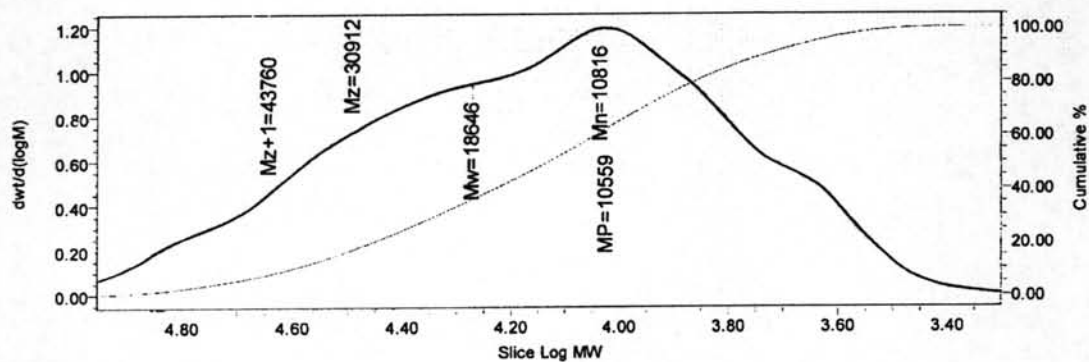


Figure B-24 GPC chromatogram of sample 10 in table 4.6: PLLA (at 120 °C, 48 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:0.5, $\overline{M}_w = 18646$

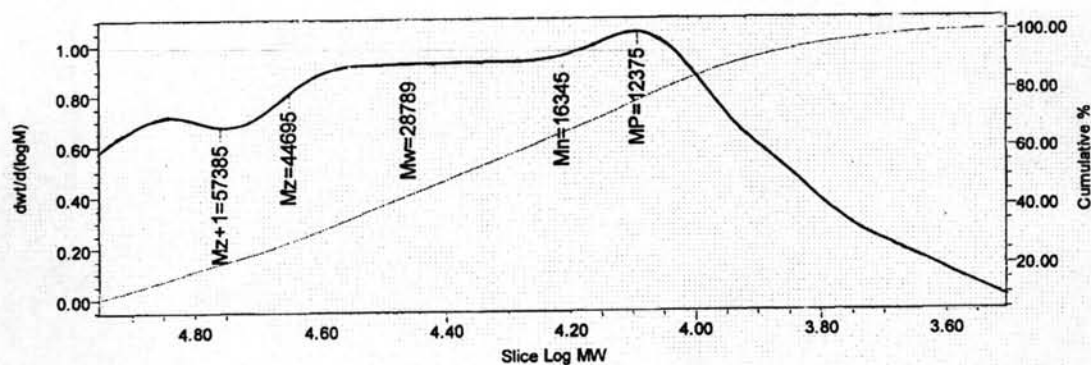


Figure B-25 GPC chromatogram of sample 11 in table 4.6: PLLA (at 120 °C, 48 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:1.1, $\overline{M}_w = 28789$

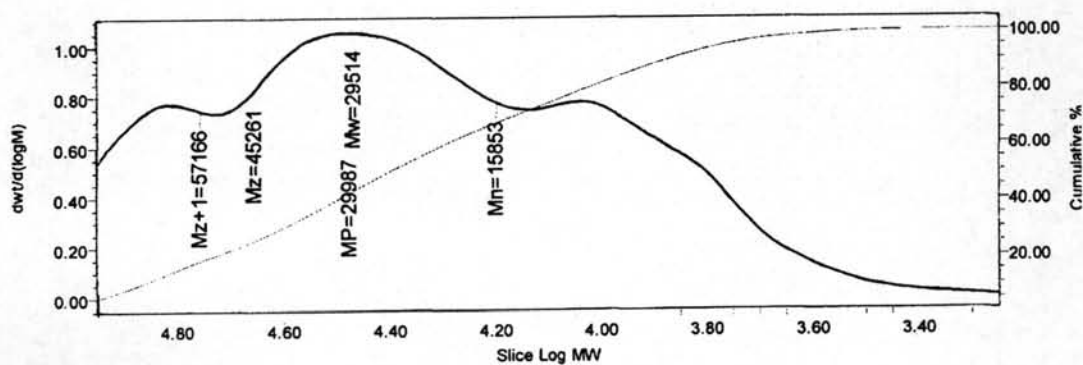


Figure B-26 GPC chromatogram of sample 12 in table 4.6: PLLA (at 120 °C, 48 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:2, $\overline{M}_w = 29514$

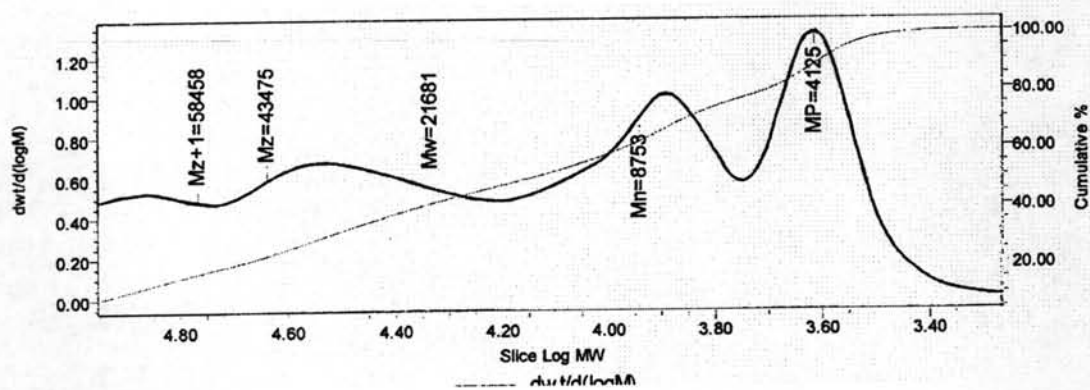


Figure B-27 GPC chromatogram of sample 14 in table 4.6: PLLA (at 120 °C, 24 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:0.5, $\overline{M}_w = 21681$

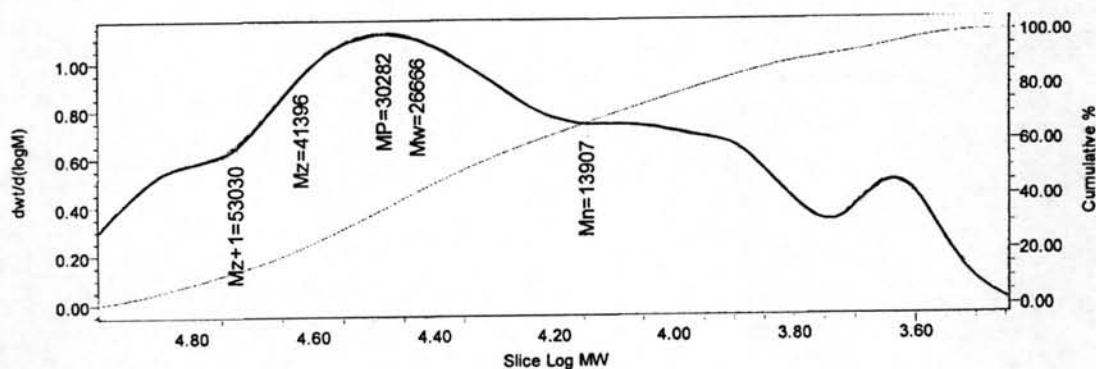


Figure B-28 GPC chromatogram of sample 15 in table 4.6: PLLA (at 120 °C, 24 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:1.1, $\overline{M}_w = 26666$

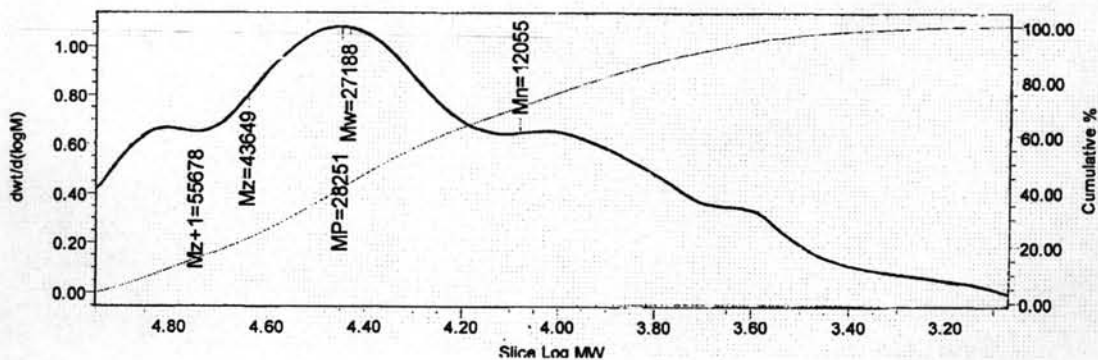


Figure B-29 GPC chromatogram of sample 16 in table 4.6: PLLA (at 120 °C, 24 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:2, $\overline{M}_w = 27188$

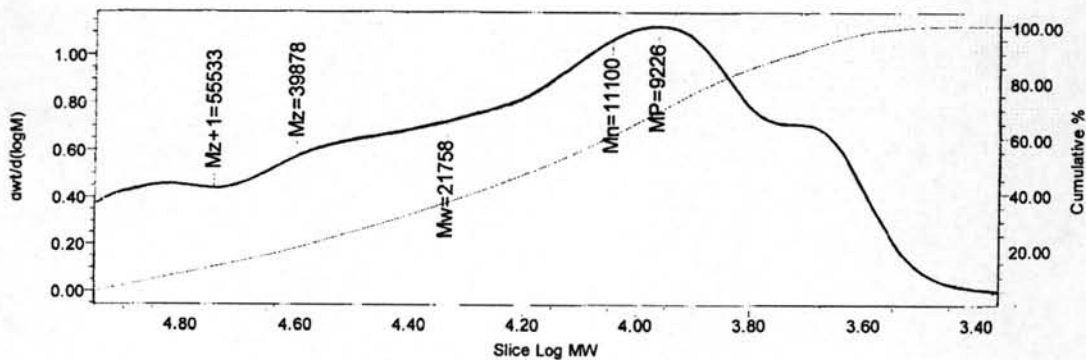


Figure B-30 GPC chromatogram of sample 18 in table 4.6: PLLA (at 120 °C, 48 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:0.5, $\overline{M}_w = 21758$

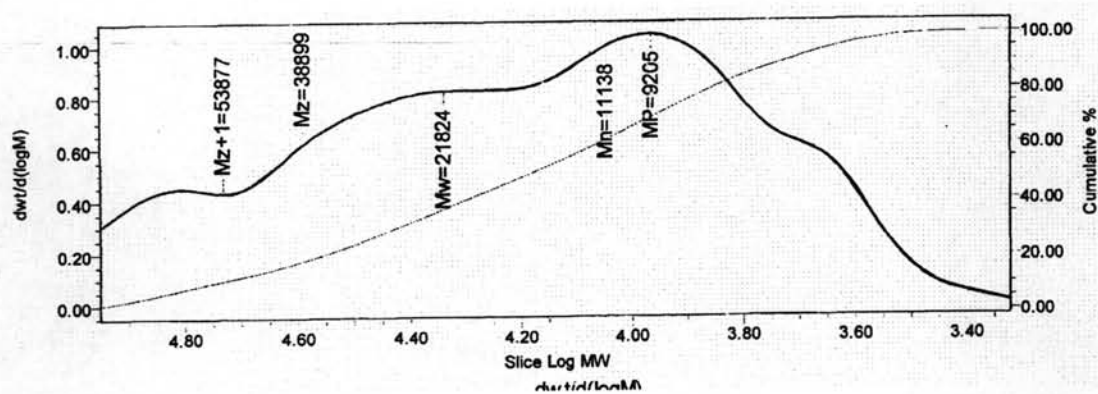


Figure B-31 GPC chromatogram of sample 19 in table 4.6: PLLA (at 120 °C, 48 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:1.1, $\overline{M}_w = 21824$

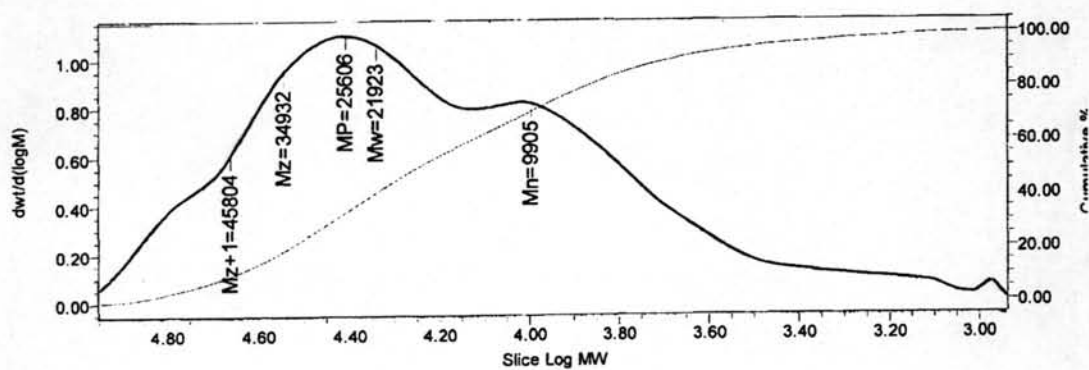


Figure B-32 GPC chromatogram of sample 20 in table 4.6: PLLA (at 120 °C, 48 hours) with tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer at the ratio of 1:2, $\overline{M}_w = 21923$

APPENDIX C

DSC chromatogram of poly(L-lactic acid)

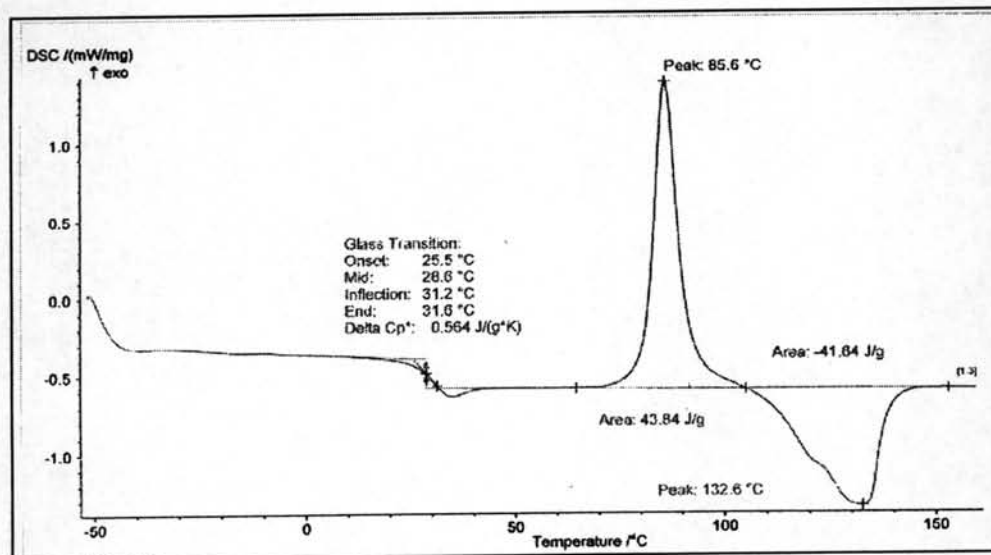


Figure C-1 DSC chromatogram of sample 9 in table 4.6: PLLA (Sn(Oct)₂, 120 °C, 48 hours), $T_g = 28.6^\circ\text{C}$

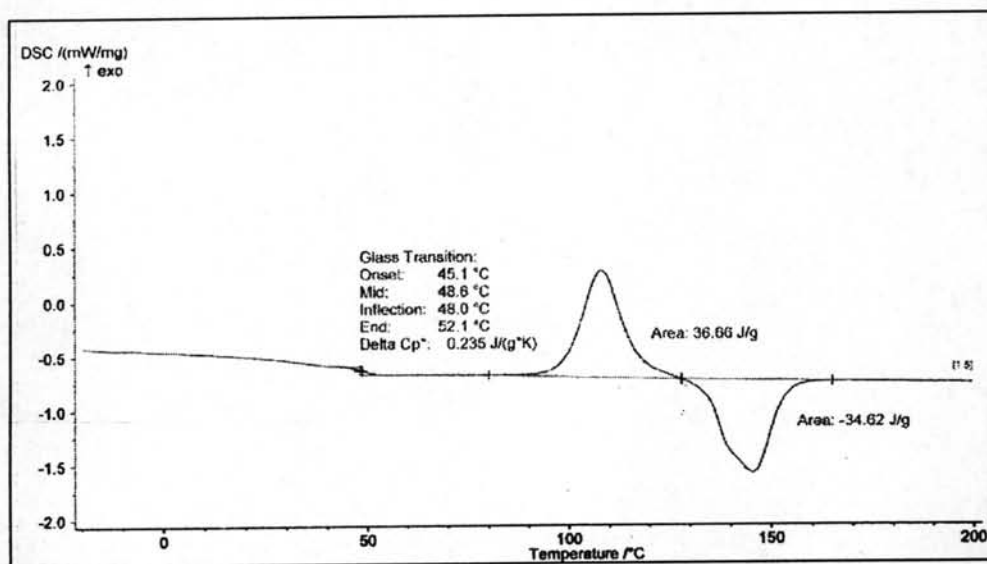


Figure C-2 DSC chromatogram of sample 10 in table 4.6: PLLA (Sn(Oct)₂, 120 °C, 48 hours) to tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer in ratio 1:0.5, $T_g = 48^\circ\text{C}$

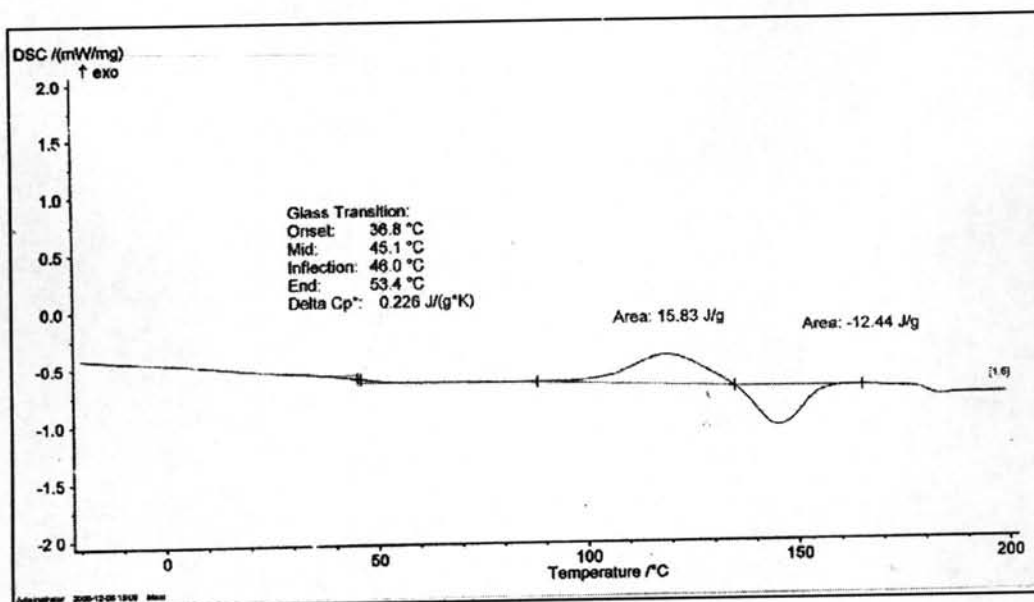


Figure C-3 DSC chromatogram of sample 11 in table 4.6: PLLA ($\text{Sn}(\text{Oct})_2$, 120 °C, 48 hours) to tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer in ratio 1:1.1, $T_g = 45.1^\circ\text{C}$.

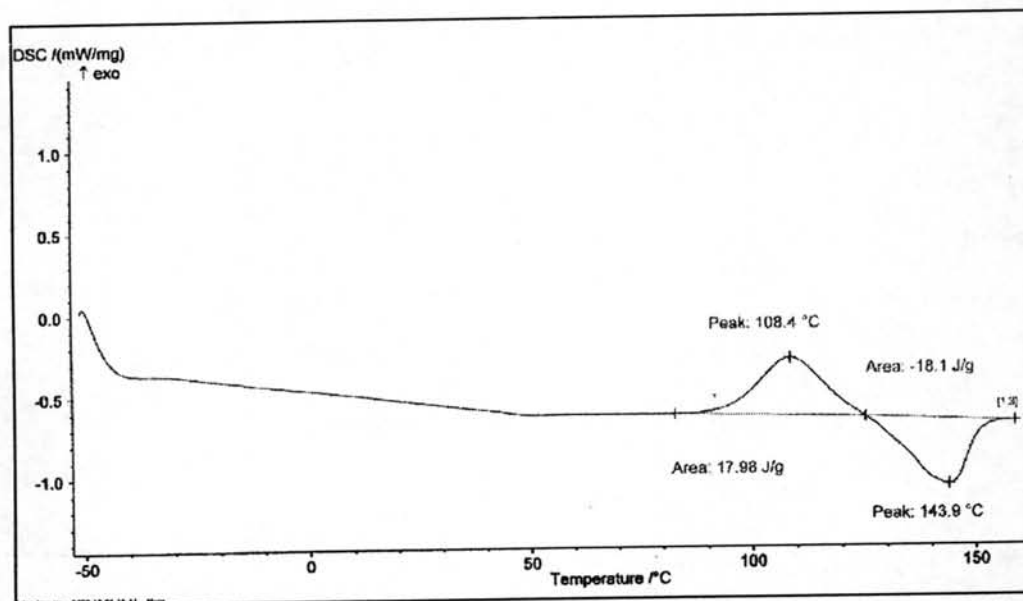


Figure C-4 DSC chromatogram of sample 12 in table 4.6: PLLA ($\text{Sn}(\text{Oct})_2$, 120 °C, 48 hours) to tolylene 2,4-diisocyanate terminated poly 1,4-butanediol prepolymer in ratio 1:2, T_g cannot be detected.

VITAE

Miss Arpudsorn Thavornwan was born in Bangkok, Thailand, on June 4th, 1981. She received Bachelor degree of science in 2003 from Department of Chemistry, Faculty of Science, Chulalongkorn University. She started as a Master degree student in program of Petrochemistry and Polymer science, Chulalongkorn University in 2004 and completed program in 2006.