

## CHAPTER V

### CONCLUSIONS AND RECOMMENDATIONS

The molecular weight of the grafting-from copolymers increased with monomer feed ratio. Among the three copolymers, PS-g-PCL showed the highest MW. PS-g-PCL and 1:1 (monomer feed weight ratio) PS-g-PLA contained some crystallinity while PS-g-Nylon6 was amorphous (like soft solid or highly viscous liquid) for all monomer feed ratios. Grafting number and average grafting length determined by NMR, weighting, and TGA-DTG increased with monomer feed ratio and, as result, enhanced amorphous structure and plasticizing effect. PS-g-PCL showed the lowest  $T_g$  (soft solid) and the lowest  $T_d$  among the three copolymers and its  $T_g$  and  $T_d$  tended to increase with increasing  $\epsilon$ -caprolactone amount. PS-g-PLA exhibited relatively high  $T_g$  and thus presented as rigid solid with moderate  $T_d$ . Moreover, PS-g-PLA exhibited increase in modulus with lactide content but its storage and loss moduli were comparable within a wide range of temperature. PS-g-PCL and PS-g-Nylon6 became softer with increasing caprolactone and caprolactam content in accordance to better solubility in water and 0.1 wt% aqueous salt solutions. On the other hand, PS-g-PLA showed better dissolution in aqueous salt solution than in water. The three copolymers were completely dissolved in chloroform (PS-g-PCL was the best) and swollen in methanol, propanol, and acetic acid (pH4).

### RECOMMENDATIONS

In synthesis, the length and number of chains depend on degree of substitution of 1-hydroxypropyl group, amount of feeding monomer, and types of catalyst. If degree of substitution of acyl group is high and reduction reaction is complete, ring opening polymerization can occur at many functional groups resulting in short grafting polymer chains. Low molecular weight PS should be easier modified than high molecular weight PS, as a result of bulky group, steric hindrance and amorphous phase. Low molecular weight PS has influence on the solubility, morphology and thermal properties. Dubois, *et al.* (1999) reported on the synthesis of

aliphatic polyester grafted starch by in situ ring-opening polymerization (ROP) of  $\epsilon$ -caprolactone in the presence of starch-like polysaccharides. The polymerization is initiated from the starch phase with the amylase/amylopectin hydroxyl functions in the presence of a catalyst such as  $\text{Sn}(\text{Oct})_2$ , or by adequate modification/activation of the surface hydroxyls into titanium or aluminium alkoxides, thereby promoting grafting and good interfacial adhesion between starch/polycaprolactone.  $\text{Sn}(\text{Oct})_2$  0.2-0.4%wt as a catalyst gives about 50%wt of ungrafted monomer, while  $\text{AlEt}_3$  gives 5-32% of ungrafted monomer.  $\text{AlEt}_3$  should be used as catalyst more than  $\text{Sn}(\text{Oct})_2$ , which is suspected on the efficiency. DR-UV results show the yellow color of all products, so the additive that shows the color like nitrobenzene (yellow), should be added in small amount.  $^1\text{H}$  NMR of nitrobenzene showed specific peak at about 8.0 ppm as confirmed by  $^1\text{H}$  NMR spectra from ChemDraw Ultra8.0 Program (Figure E1) and DR-UV results show samples absorbing light in purple to blue ranges.

$^{13}\text{C}$  NMR of all samples show unclear peak because the running period was about 2-3 hrs, which was too short. High molecular weight polymers generally need  $^{13}\text{C}$  NMR run over night to show clear peak.

The solubility of copolymers depends on the sense of observation of individual observer. In this experiment, the number of solvent drops into copolymer were counted. A cylinder was used to determine the number of solvent drops in 1 mL which was only a rough scale. The copolymers were dissolved in water and 0.1% salt water for 1 day with only a small amount of low molecular weight polymer coming out. If the copolymers were dissolved in these solvents for over 1 day, higher amount of low molecular weight polymer may come out.

Thermal properties of copolymers determined with DMA were carried out with only PS-g-PLA. Melt rheology analysis should be carried out with PS-g-PCL and PS-g-Nylon6 to confirm the DSC results because both of them were gel-like and thus not suitable for DMA test.

Grafting percentage calculation by all methods (weight, weight loss by TG-DTA, and the number of protons by  $^1\text{H}$  NMR spectrum) gave the same trend. Counting number of protons by  $^1\text{H}$  NMR spectrum was the best method because it showed the accurate value compared in atomic level. The calculations, based on

weighing and weight loss by TG-DTA, showed higher error percentage from the weight of contaminating substances, e.g. nitrobenzene and oligomers. Contaminating nitrobenzene was proved by  $^1\text{H}$  NMR spectrum that appeared at about 8.0 ppm. Castle, *et al.* (2004) analyzed honey samples for residues of nitrobenzene and petroleum from the possible use of flow mixture in hives. The results show boiling point of nitrobenzene at about 211°C. Then degradation peak of nitrobenzene may be buried in the degradation peak of grafting polymer, the calculation could contain mistake too.

The copolymers can be spun to fiber and make a good film. Therefore PS-g-PLA and PS-g-PCL could be applied to coat agriculture products, e.g. orange, mangosteen, etc., because PLA and PCL are biodegradable polymers. Moreover, these copolymers could be applied to mulch film, used for preventing the humidity of soil. Furthermore, PS-g-Nylon6 in the ratio 1 to 3 was in the form of very soft and sticky solid which can be modified to glue. Also, when grafting of biocompatible polymer percentage was increased. the copolymers were softer. This advantage was suitable to improve the specific plastic used in medical applications such as flexible tube, or disposal tube. Solution of color for nail coating can be developed by adding copolymers that are clear film and able to wash out easily by water.

## REFERENCES

- Capek, I., Nguyen, S.H., and Berek, D. (2000) Polystyrene-graft-poly(ethylene oxide) copolymers prepared by macromonomer technique in dispersion. 2. Mechanism of dispersion copolymerization. Polymer, 41, 7011-7016.
- Chen, C.C., Chueh, J.Y., Tseng, H., Huang, H.M., and Lee, S.Y. (2003) Preparation and characterization of biodegradable PLA polymeric blends. Biomaterials, 24, 1167-1173.
- Chen, L., Ni, Y., Bian, X., Qiu, X., Zhuang, X., Chen, X., and Jing X. (2004) A novel approach to grafting polymerization of  $\epsilon$ -caprolactone onto starch granules. Carbohydrate Polymers, 337, 1-7.
- Cretua, A., Gattina, R., Brachaisa, L., and Barbier-Baudrya D. (2004) Synthesis and degradation of poly (2-hydroxyethyl methacrylate)-graft-poly ( $\epsilon$ -caprolactone) copolymers. Polymer Degradation and Stability, 83, 399–404.
- Davis, R.D., Gilman, J.W., and VanderHart, D.L. (2003) Processing degradation of polyamide6/montmorillonite clay nanocomposites and clay organic modifier. Polymer Degradation and Stability, 79(1), 11-121.
- Dubis, E.N., Dubis, A.T., and Morzycki, J.W. (1999) Comparative analysis of plant cuticular waxes using HATR FT-IR reflection technique. Journal of Molecular Structure, 511-512, 173-179.
- Dubois, P., Krishnanb, and M. and Narayanb, R. (1999) Aliphatic polyester-grafted starch-like polysaccharides by ring-opening polymerization. Polymer, 40, 3091–3100.
- Edlund, U., and Albertsson, A.-C. (2003) Polyesters based on diacid monomers. Advanced Drug Delivery Reviews, 55, 585-609.
- Franco, C.R., Cyras, V.P., Busalmen, J.P., Ruseckaite, R.A., and Vazquez, A. (2004) Degradation of polycaprolactone/starch blends and composites with sisal fibre. Polymer Degradation and Stability, 86, 95-103.
- Hesse, M., Meier, H., and Zeeh, B. (1991) Spektroskopische Methoden in der organischen Chemie. Georg Thieme Verlag, Stuttgart.

- Huang, M.H., Li, S., and Vert, M. (2004) Synthesis and degradation of PLA-PCL-PLA triblock copolymer prepared by successive polymerization of  $\epsilon$ -caprolactone and DL-lactide. Polymer, 45, 8675-8681.
- Janata, M., Masař, B., Toman, L., Vlček, P., Polická, P., Brus, J., and Holler, P. (2001) Multifunctional ATRP macroinitiators for the synthesis of graft copolymers. Reactive & Functional Polymers, 50, 67-75.
- Janata, M., Masař, B., Toman, L., Vlček, P., Polická, P., Látalová, P., Brus, J., and Holler, P. (2003) Synthesis of novel types of graft copolymers by a “grafting-from” method using ring-opening polymerization of lactones and lactides. Reactive & Functional Polymers, 57, 137-146.
- Jeon, H.K., Feist, B.J., Koh, S.B., Chang, K., Macosko, C.W., and Dion, R.P. (2004) Reactively formed block and graft copolymers as compatibilizers for polyamide 66/PS blends. Polymer, 45, 197-206.
- Jiang, T., Wang, Y., Yeh, J., and Fan, Z. (2005) Study on solvent permeation resistance properties of nylon6/clay nanocomposite. European Polymer Journal, 41, 459-466.
- Kee, R.A., and Gauthier, M. (2002) Arborescent Polystyrene-graft-poly(2-vinylpyridine) Copolymers: Synthesis and Enhanced Polyelectrolyte Effect in Solution. Macromolecules, 35, 6526-6532.
- Kohori, F., Sakai, K., Aoyaki, T., Yokoyama, M., Sakurai, Y., and Okano, T. (1988) Preparation and characterization of thermally responsive block copolymer micelles comprising poly(N-isopropylacrylamide-b-DL-lactide). Journal of controlled release, 55, 87-98.
- Li, F., Chen, Y., Zhu, W., Zhang, X., and Xu, M. (1998) Shape memory effect of polyethylene/nylon6 graft copolymers. Polymer, 39(26), 6929-6934.
- Li, J., and Gauthier, M. (2001) A Novel Synthetic Path to Arborescent Graft Polystyrenes. Macromolecules, 34, 8918-8924.
- Li, J., Gauthier, M., and Teertstra, S.J. (2004) Synthesis of Arborescent Polystyrene-graft-polyisoprene Copolymers Using Acetylated Substrates. Macromolecules, 37, 795-802.

- Liu, Y., Tian, F., and Hu, K.A. (2004) Synthesis and characterization of a brush-like copolymer of polylactide grafted onto chitosan. Carbohydrate Reserch, 339, 845-851.
- Maio, E.O., Iannance, S., Sorrentino, L., and Nicolais, L. (2004) Isothermal crystallization in PCL/clay nanocomposites investigated with thermal and rheometric methods. Polymer, 45, 8893-8930.
- Matzer, M., Schober, D.L., and McGrath, J.E. (1973) Polystyrene-nylon6 graft copolymers. European Polymer Journal, 9(6), 469-480.
- Nojima, S., Akutsu, Y., Washino, A., and Tanimoto, S. (2004) Morphology of melt-quenched poly( $\epsilon$ -caprolactone)-block-polyethylene copolymers. Polymer, 45, 7317-7324.
- Nojima, S., Hashizume, K., Rohadi, A., and Sasaki, S. (1997) Crystallization of  $\epsilon$ -caprolactone blocks within a crosslinked microdomain structure of poly( $\epsilon$ -caprolactone)-block-polybutadiene. Polymer, 38(11), 2711-2718.
- Perlovskaya, O.R., Shilina, M.I., and Smirnov, V.V. (2001) Aluminium Chloride Complexes with Nitrobenzene: Low-Temperature Synthesis, Structure, and Stability. Russian Journal of Coordination Chemistry, 27(7), 469-475.
- Pramoda, K.P., Liu, T., Liu, Z., He, C., and Sue, H.J. (2003) Thermal degradation behavior of polyamide6/clay nanocomposites. Polymer Degradation and Stability, 81, 47-56.
- Schaller, Ch., Schaner, T., Dirnberger, K., and Eisenbach, C.D. (1999) Synthesis and properties of hydrophobically modified water-borne polymers for pigment stabilization. Progress in Organic Coatings, 35, 63-67.
- Shibata, J., Fujii, K., Murayama, N., and Yamamoto, H. (2002) Dispersion and Flocculation Behavior of Fine Metal Oxide Particles in Various Solvents. KONA, 20, 263-269.
- Sivalingam, G., Karthik, R., and Madras, G. (2003) Kinetics of thermal degradation of poly( $\epsilon$ -caprolactone). Journal of Analysis Application Pyrolysis, 70, 631-647.
- Sivalingam, G., and Madras, G. (2004) Thermal degradation of binary physical mixtures and copolymers of poly( $\epsilon$ -caprolactone), poly(D,L-lactide), poly(glycolide). Polymer Degradation and Stability, 84, 393-398.

- Slomkowski, S., Sosnowski, S., and Gadzinowski, M. (1998) Polyester from lactides and  $\epsilon$ -caprolactone. Disperion polymerization versus polymerization in solution. Polymer Degradation and Stability, 59(1-3), 153-160.
- Slomkowski, S., Sosnowski, S., and Gadzinowski, M. (1999) Latexes and microspheres by ring-opening polymerization of cyclic esters. Colloids and Surfaces, 153, 111-118.
- Tajouri, T. Bouchriha, H., and Hommel, H. (2003) Solvent and temperature effects on chain conformations in interfaces of polymer grafted on silica. Study by  $^1\text{H}$  NMR. Polymer, 44, 6825-6833.
- Tomita, K., Nakajima, T. Kikuchi, Y., and Miwa, N. (2004) Degradation of poly(L-lactic acid) by a newly isolated thermophile. Polymer Degradation and Stability, 84, 433-438.
- Wu, Y., Zheng, Y., Yang, W., Wang, C., Hu, J., and Fu, S. (2005) Synthesis and characterization of a novel amphiphilic chitosan-poly lactide graft copolymer. Carbohydrate Polymers, 59, 165.