SEGMENTAL COPOLYMERS OF CONDENSATION POLYESTERS AND POLYLACTIDE


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Introduction

Polylactide polymers have attracted enormous attention as a replacement for conventional synthetic packing materials. The most common products based on L-lactide are stiff and brittle and need modifications for most practical applications [1]. The typical approach involves the use of plasticizers, blending with other biodegradable materials or ring opening copolymerization of L-lactide with heterocyclic monomers. Another interesting possibility is to obtain block copolymers consisting of stiff polylactide segments combined with elastic segments prepared by polycondensation [2]. In this work several materials of this architecture have been obtained by bulk polymerization of L-lactide in the presence of tin(II) 2-ethylhexanoate and polyester diols as coinitiators and chain transfer agents to determine factors affecting the miscibility of both segments in amorphous phase and select the polyesters that can serve either as plasticizers or impact modifiers for commercial polylactides.

Results and Discussion

The polyester segments were obtained by ester interchange reactions using dimethyl adipate, dimethyl carbonate, dimethyl terephthalate, 1,4-butanediol, 1,3-propanediol and ethylene glycol as starting materials in the presence of tin(II) 2-ethylhexanoate as catalysts. In the first step run at 100-150 °C, methanol was continuously distilled off. In the second step the temperature was raised to about 200 °C and excess of diols and side cyclic products were removed under vacuum. Using this methodology the library of polyesters terminated by hydroxyl group of Mₙ in the range 1-9×10³ was obtained. Their composition and average number molecular weight (Mₙ) were determined by means of ¹H-NMR and MALDI ToF analysis. The DSC studies revealed that most of the polyesters based on multi component systems are amorphous or slightly crystalline materials of glass transition temperature in the range 200-250 K.

In the next step the solution of tin(II) 2-ethylhexanoate in oligomeric diols was mixed with L-lactide and heated at 180°C for 3 h. Under these conditions the polymerization of lactide occurred effectively and the monomer conversion was typically about 92-95%. The crude products were purified by dissolving in methylene dichloride and precipitation with methanol. The ¹H-NMR spectra of purified products (Fig. 1) indicate that after polymerization the signal characteristic for terminal CH₂OH groups in oligomeric

Figure 1. The ¹H-NMR spectra of triblock copolymer PLA-PPBATC-PLA.
polyesters disappeared which strongly suggests the incorporation of condensation polymers into the polylactide chains. The average number of lactide monomeric units per one segment of copolyester was varied from 9 to about 430 which corresponds to $M_n$ in the range $9\times 10^3$ to $70\times 10^3$.

The polydispersity of the studied samples determined by GPC method was typically around 2. The fractionation of some samples was performed using GPC columns by collecting small portions (10 drops) of eluate. It turned out that the compositions of fractions do not differ significantly ($\pm 10\%$) and thus we believe that the concentration of polylactide homopolymers in this system is negligible. The DSC studies showed that segmental polyesters consisting of polylactide and polyesters bearing adipic and carbonic acid units exhibit one glass transition temperature, whereas the introduction of terephthalic units leads to separation of the amorphous phase into two domains of different flexibility (Fig. 2 A and B).

![DSC thermogram of: (A) macroinitiator PPAC (B) macroinitiator PPBATC and their triblock copolymers obtained by subjecting to ROP of lactide.](image)

Attempts were also made to obtain statistical copolymers by transesterification of polymer chains at higher temperature. The process of segmental exchange was clearly observed at temperature exceeding $200\,^\circ\text{C}$ but was accompanied by the backbiting reactions leading to evolution of substantial amount of lactide monomer.

The effect of both types of segmental copolymers on mechanical properties of commercial poly(L-lactide) (Nature Works) and its blend with polyesters based on terephthalic and adipic acids polyesters are currently studied and the results of these studies will be discussed during the conference.

**Conclusion**

We have demonstrated that the bulk polymerization of lactide in the presence of condensation polyesters terminated by hydroxyl group gives an easy access to segmental polymers which might be useful components of biodegradable materials based on polylactides.

**References**

2. Ch. Ba, J. Yang; Q. Hao; X. Lin; A. Cao Biomacromolecules 2003, 4, 1827