BIODEGRADATION OF LINEAR BLOCK COPOLYMERS CONTAINING POLY(LACTIC ACID) SEGMENTS

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ABSTRACT

Poly(lactic acid) (PLA) undergoes enzymatic or non-enzymatic hydrolysis when it is exposed to an aqueous environment.[1] Many kinds of enzymes have been isolated and purified for biodegradable PLA. Proteinase K shows strong effects on the degradation of PLA and its copolymers, which was presented by Williams.[2] The biodegradation rate of polyesters correlates with their chemical structure, hydrophobic-hydrophilic balance of the polymeric backbone, molar mass and the degree of crystallinity. In case of aliphatic polyesters the difference between temperature of melting point of polyester and biodegradation process is also important. If the difference is lower than 30°C, the degradation occur fast.[4] The presence of longer aliphatic domains, e.g., in block copolyesters does not facilitate the hydrolytic attack by the enzyme, but longer aromatic sequences, which control the melting point of the crystalline regions and reduce the biodegradation rate.[5]

In this research we synthesized PLA block copolymers via ring opening polymerization of L-lactide (L-LA) in the presence of various types of polyesterdiols and polyestercarbonatediols obtained from 1,4-butanediol, 1,3-propanediol and dimethyl esters of adipic, terephthalic and carbonic acids. The reactions were carried out in bulk at 190°C in the presence of tin (II) 2-ethylhexanoate as a catalyst led to the formation of a mixture of polylactide (PLLA) and block copolymers of L-LA with the macrodiols applied. DSC analysis confirmed that PLA and aliphatic polyester segments are homogeneous in amorphous domains, whereas the aliphatic-aromatic components exhibit phase separation with PLA blocks. In the next step, thin copolymers films were incubated in buffered aqueous solution of proteinase K. Degradation was followed by weight loss and various analytical techniques such as ^{1}H NMR, GPC and DSC were applied. It turned out, that copolymers containing terephthalic units in their structure degrade very slowly (50% after 7 days), because of low mobility of chains and high melting point. On the basis of ^{1}H NMR spectrum it was proved that segment of PLLA degrade faster than aliphatic-aromatic middle segment. In contrast, the copolymer with aliphatic polyester segment degraded very fast. The copolymer obtained in the presence of poly(butylene adipate) (PBA) or poly(propylene-co-butylene adipate-co-carbonate) (PPBAC) decompose in almost 90% after 7 days. In this case, PLA units exhibit lower degradation rate than PBA and PPBAC segments. Moreover, the presence of carbonate bonds in copolymer chains slightly decreases the rate of degradation.

References:

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