# Crosslinking Characteristics and Shape Memory Effect of a Biodegradable Multiblock Copolymer Poly(propylene fumarate)-*co*-Poly(ε-caprolactone)

Shanfeng Wang, Lichun Lu, James A. Gruetzmacher, Kee-won Lee, Bradford L. Currier, Michael J. Yaszemski
Tissue Engineering and Polymeric Biomaterials Laboratory, Departments of Orthopedic Surgery and Biomedical Engineering, Mayo Clinic College of Medicine, Rochester, MN 55905

**Introduction:** Recently a novel crosslinkable and biodegradable copolymer poly(propylene fumarate-*co*-caprolactone) (PPF-*co*-PCL) with 15 compositions has been synthesized (Scheme 1) to obtain controllable physical properties to satisfy various needs in tissue engineering, particularly, bone and nerve regenerations.[1] The physical properties have been extensively investigated and an important characteristic temperature $T_g$, i.e., glass transition temperature decreases progressively with increasing the PCL composition in the copolymer.[1] The biodegradation rate and mechanical properties can therefore be well modulated by the different molecular structure, copolymer composition, and crosslinking density. In this study, the crosslinking characteristics and biodegradation of PPF-*co*-PCL copolymers using both chemical crosslinking and photo-crosslinking methods have been investigated in detail. Furthermore, the shape-memory effect has been revealed when the composition of PCL is high enough to show the crystallinity in the copolymers.
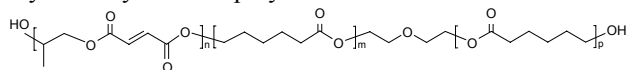


**Scheme 1**

**Methods:** PPF-*co*-PCL was produced as described previously.[1] Fifteen copolymers with a variety of PCL compositions ranging from 29% to 90% were crosslinked by chemical crosslinking or photocrosslinking methods. The weight-average molecular weights of the copolymers are between 8,230 and 47,100 g mol$^{-1}$ determined by GPC using monodisperse polystyrene standards. In thermal-crosslinking process, benzoyl peroxide (BPO) and *N*-dimethyl toluidine (DMT) were used as the free radical initiator and accelerator, respectively. 100 µL of initiator solution (50 mg of BPO in 250 µL of NVP) and 40 µL of accelerator solution (20 µL of DMT in 980 µL of methylene chloride) were added in 1.5 g PPF-*co*-PCL solution in 500 µL of methylene chloride and mixed thoroughly. The polymerizing scaffold was transferred into various Teflon molds and the molds were placed in a convection oven overnight to facilitate crosslinking. After crosslinking, the crosslinked polymer was removed from the mold after it was cooled to ambient temperature. Photocrosslinking were initiated with UV (λ=315-380 nm) using a photoinitiator bisacylphosphine oxide (BAPO). The mixture was poured in a mold formed by two glass plates and a Teflon spacer of 1 mm thickness and the mold was placed directly under UV light for 30 min to facilitate crosslinking. The gel fraction and swelling ratios in various solvents were determined and the thermal properties were measured by DSC and TGA. The mechanical properties including compression modulus, flexibility, surface rigidity, and pulling strength have been tested.

**Results/Discussion:** The copolymers were found to be both self-crosslinkable without using a crosslinker and photo-crosslinkable. As shown in Fig. 1, a typical scaffold can be made using the method of 3D printing and injection molding. The pore size of the copolymer scaffold is 600 µm and the wall thickness is 500 µm. It can be seen in Fig.2a that only one broad glass transition exists for the crosslinked copolymers when PCL content is higher than 54%. No discernible glass transition was found for higher PPF compositions as the result of high crosslinking density. The glass transition temperature for the crosslinked copolymers decreases with increasing PCL composition. PCL is a semi-crystalline copolymer; however, the crystallinity was suppressed efficiently first by PPF segments and then crosslinks. Only the highest PCL composition of 90% shows a very slight crystalline peak at 17.1 °C. The amorphous characteristics of the crosslinked copolymers allow faster degradation of the material and give transparent products. TGA results in Fig.2b show there is only one degradation step for all the crosslinked copolymers. The thermal stability increases with the PCL composition. Thermal degradation temperature increases from 332 to 390 °C when the PCL composition increases from 30% to 90%.
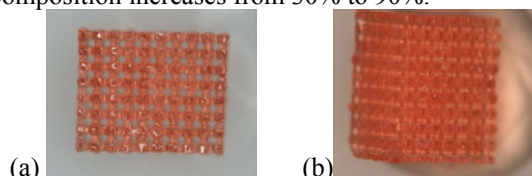


(a)          (b)

**Fig. 1:** Porous structure of a typical copolymer scaffold made using 3D printing method.
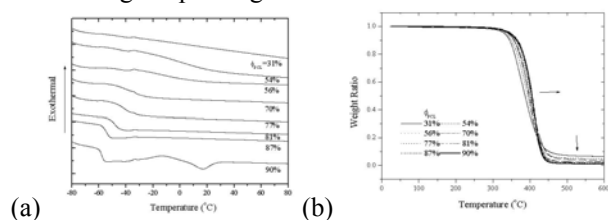


(a)          (b)

**Fig.2:** (a) DSC and (b) TGA curves of the photo-crosslinked copolymers with various compositions.

**Conclusions:** The crosslinking characteristics of PPF-*co*-PCL have been investigated. The thermal properties and degradation information will help advance its tissue engineering applications.

**References**

1. Wang SF. Macromolecules 2005;38:7358.

**Acknowledgments**