Absorbable Swellable Monofilament Fibers: A Preliminary Report

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Introduction: It is widely acknowledged that swellable synthetic polymers can be prepared by the covalent crosslinking of water-soluble polymers forming what is known in the industry as the precursors to hydrogels[1]. Additionally, the concept of using amphiphilic, liquid copolyesters with chains comprising covalently linked hydrophilic and hydrophobic segments/blocks to produce swellable polymeric materials, or hydrogels, through the non-covalent association of the hydrophobic blocks in the presence of water was disclosed recently[2,3]. Although these polymers are promising candidates for many biomedical applications because of their favorable interaction with the biological environment, they lack the structural mechanical properties needed to form solid products such as surgical implants, coatings for certain surgical implants, or carriers for the delivery of bioactive agents that require high levels of structural integrity. Traditionally, these requirements have been met with the use of crystalline absorbable polyesters based on one or more monomers such as glycolide, lactide, and ε-caprolactone. Although used in many biomedical applications because of their high biocompatibility and biodegradation, these materials are essentially hydrophobic thus rendering them less suitable for applications where a more intimate biological interaction is desired. Such interactions may include swelling-driven space-filling, modulated delivery of bioactive agents, enhanced wetability, and accelerated hydrolysis. The concept of using crystalline, amphiphilic copolymers comprising a central hydrophilic poly(ethylene oxide) block covalently linked to two hydrophobic polyester blocks to prepare absorbable swellable fibers was recently reported[4]. This communication addresses the preparation and characterization of such amphiphilic copolymers and their conversion to and evaluation as absorbable swellable monofilament fibers.

Materials and Methods:

• **Polymer and Fiber Preparation:** High molecular weight, fiber-forming, crystalline, amphiphilic copolymers were prepared by the end-grafting of poly(ethylene glycol) (PEG) with one or more cyclic monomers selected from the group consisting of *l*-lactide, glycolide, trimethylene carbonate, and ε-caprolactone as described elsewhere[4]. The copolymers were devolatilized to remove any residual monomer, melt extruded into monofilament fibers, and oriented. The mechanical properties of the fibers were evaluated using an MTS Synergie 200 Universal Tester.

• **Evaluation of Swelling Properties of Monofilaments:** The percent cross-sectional area increase of the monofilaments was calculated by measuring the change in diameter using an optical micrometer and microscope after incubation in a 7.2 pH phosphate buffer at 37°C or isotonic saline at 25°C for predetermined time periods.

Results and Discussion: The properties of six crystalline amphiphilic copolymers with varying amounts of PEG-based components are summarized in Table I. The data demonstrate that high molecular weight amphiphilic copolymers can be prepared with PEG levels up to 37 weight percent. The relative copolymer molecular weights as indicated by their inherent viscosities are essentially inversely proportional to their PEG content. All copolymers exhibited a T_m around 50°C which indicates that the PEG blocks are able to crystallize along with the polyester blocks. Properties of monofilament fibers prepared from the amphiphilic copolymers are given in Table II. The data demonstrate that all copolymers can be converted to monofilament fibers with high tensile strengths. The swellability of the fibers is essentially proportional to their PEG content with cross-sectional area increases ranging from 20% to 74% in a simulated biological environment.

Table I. Properties of Amphiphilic Copolymers

Copolymer	PEG wt%	Major Monomeric Precursors[a]	I.V.[b] dL/g	T_m, °C	ΔH, J/g
A	18	G, CL	(1.62)	52, 214	11, 42
B	23	L, CL	1.28	45, 159	10, 38
C	25	L, TMC	1.16	53, 143	27, 22
D	27	L, TMC	0.96	53, 172	14, 34
E	37	L, TMC	0.86	53, 151	39, 23

[a]G = glycolide; CL = ε-caprolactone; L = *l*-lactide; TMC = trimethylene carbonate
[b]Inherent viscosity in $CHCl_3$ (in HFIP)

Table II. Properties of Swellable Monofilaments

Fiber from Copolymer:	A	B	C	D	E
Diameter, mm	0.43	0.29	0.13	0.23	0.10
Modulus, Kpsi	172	345	239	453	190
Elongation, %	53	91	44	73	99
Knot Max Load, N	31.9	17.3	2.6	16.3	-
Cross-sectional Increase, % at 10 min.	-	-	-	-	37[b]
60 min.	20[a]	28[a]	-	57[a]	74[b]
16 hrs.	-	-	72[a]	-	-

[a]In 7.2 pH phosphate buffer at 37°C
[b]In isotonic saline at 25°C

Conclusions: Fiber-forming amphiphilic crystalline copolymers have been prepared and converted by melt-spinning to monofilament fibers with unique properties conducive to increased biological interaction.

References:

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