Flexible, elastic and tear-resistant networks prepared by photo-crosslinking poly(trimethylene carbonate) macromers

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Abstract

Poly(trimethylene carbonate) (PTMC) macromers with molecular weights \( M_n \) between 1000 and 41,000 g mol\(^{-1} \) were prepared by ring opening polymerization and subsequent functionalization with methacrylate end groups. Flexible networks were obtained by radical photo-crosslinking reactions of these macromers. With increasing molecular weight of the macromer the networks obtained showed increasing swelling ratios in chloroform and decreasing glass transition temperatures, reaching a constant value of approximately \( -18^\circ C \), which is close to that of linear high molecular weight PTMC. For all prepared networks the creep resistance was high. However, the molecular weight of the macromer strongly influenced the tensile properties of the networks. With increasing molecular weight of the macromer the E-modulus of the networks decreased from 314 MPa (lowest \( M_n \)) to 5 MPa (highest \( M_n \)), while their elongation at break continuously increased, reaching a very high value of 1200%. The maximum tensile strength values of the networks were found to first decrease with increasing \( M_n \) but to increase again at values above approximately 10,000 g mol\(^{-1} \), at which the networks started to show rubber-like behavior. The toughness (area under the stress–strain curves, \( W \)) determined in tensile testing experiments, in tear propagation experiments, and in suture retention strength measurements showed that PTMC networks prepared from the higher molecular weight macromers (\( M_n > 10,000 \) g mol\(^{-1} \)) were tenacious materials. The mechanical properties of these networks compare favorably with those of linear high molecular weight PTMC and well-known elastomeric materials like silicone rubber (poly(dimethylsiloxane)) and natural latex rubber. Additionally they also compare well with those of native blood vessels, which may be of importance in the use of these materials for the tissue engineering of small diameter blood vessels.

1. Introduction

Much attention has recently been paid to developing biodegradable elastic materials for the preparation of soft tissue implants and soft tissue engineering scaffolds for use in cardiovascular applications. As suturing is the most common technique to connect grafts to soft tissue the materials are ideally suturable and resistant to tearing [1–3]. When suturing a defect is created that in a two step tearing process can lead to catastrophic failure of the implant [4]. Nevertheless, research on developing suturable tough and tear-resistant biodegradable elastomeric implant materials is very limited.

We have prepared flexible and elastic creep-resistant networks that are biocompatible and biodegradable from high molecular weight poly(trimethylene carbonate) (PTMC). The polymer crosslinks when exposed to \( \gamma \)-irradiation, and stable networks with excellent mechanical properties, elasticity, and resistance to creep can be obtained in this manner [5,6]. Elastic porous PTMC structures for use in vascular tissue engineering could be prepared in this way [7]. However, the crosslinking procedure is quite involved as \( \gamma \)-irradiation of the polymers needs to be carried out externally in a specialized facility. Photo-crosslinking of precursor macromers would be a much more practical and versatile approach to prepare tear- and creep-resistant PTMC networks.

In early work by Storey et al. [8] three-armed oligomeric polyesters based on \( \alpha,\beta \)-lactide and trimethylene carbonate with