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# Functionalization of biodegradable aliphatic polyesters by direct methylenation and thiol-ene reaction

**Takao Aoyagi, Hiroshi Yamashita, Kohei Iwamatsu** and **Toru Hoshi**
Nihon University, JAPAN

Aliphatic polyesters, especially, PGA, PLA, PCL and their copolymers have withdrawn much attention as biodegradable polymeric materials. Among them, we are dealing with PCL as a smart material and have already reported their temperature-responsive surface shape memory properties. They could contribute to mechano-biological studies because they can modulate elasticity and viscosity by only temperature change. Furthermore, drug permeation control near body temperature could succeed by effective melting point modulation by macromonomer design. Recently, we have studied two types of functionalizing methods of PCL-based materials. The project image is shown in Figure 1. One is macromonomer that has both cationic moieties and cross-linkable groups. Other is direct methylenation of the PCL main chains. The methylene groups were promising for further functionalization by thiol-ene addition reaction. To achieve first purpose, we newly designed branched PCL macromonomers which have bromomethyl groups at the of chain ends. Then, these terminal bromomethyl groups reacted with 2, 2'-dimethylaminoethyl methacrylate to afford the objective macromonomer as seen in Figure 1. The corresponding macromonomer solution was cast and UV light was irradiated in the presence of photo-sensitizer to obtain the cross-linked PCL membrane. This materials show positive charge and those values can be controlled by temperature change. Additionally they possess shape memory properties. For the second subject, dimethyltitanocene was applied for direct methylenation of PCL. This compound is well known to work effective methylenation for low-molecular-weight carbonyl compounds such as aldehyde, ketone and ester. Following thiol-ene reactions using thioglycolic acid, aminoethanethiol hydrochloride or mercaptoethanol were carried out for further functionalization of methylenated PCL. Such functional PCL-based polymeric materials are expected to interact to proteins, living cells or tissues and are promising for highly functional biodegradable materials.

## Biography

Takao Aoyagi is a professor of Department of Materials and Applied Chemistry of Nihon University in Tokyo, Japan. He received his PhD at Tokyo Institute of Technology in 1993. After finished Graduate School of Science and Engineering of Waseda University, he belonged to a Japanese chemical company (Lion Corporation, 1986-1987) and private institute (Sagami Chemical Research Center, 1987-1995). He became an assistant professor at Institute of Biomedical Engineering in 1995 and associated professor in 2001, Tokyo Women's Medical University. In 2002, he was promoted to full Professor of Department of Nanostructure and Advanced Materials of Kagoshima University. In 2009, he moved to the Biomaterials Center and Coordinating Director of Nanotech-driven Materials Research for Biotechnology, National Institute for Materials Science (NIMS) in Tsukuba, Japan. His recent research field is design of smart biomaterials for biomedical applications.

aoyagi.takao@nihon-u.ac.jp

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