

# Soft segment composition and its influence on phase-separated morphology of PCL/PEG-based poly(urethane urea)s

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**Abstract** A composition-dependent microphase separation of segmented poly(urethane urea)s (PUUs), based on a mixture of two hydrophobic (polycaprolactone) and hydrophilic (polyethylene glycol) polyols, is investigated. Synthesis of PUUs was carried out through the reaction of in situ generated AB-type macromonomers, prepared from the reaction of NCO-terminated urethane prepolymers, with benzoic acid in dimethyl sulfoxide as solvent/reagent at 40–80 °C. The segmented PUUs were characterized by different methods including FTIR and NMR spectroscopies, gel permeation chromatography, differential scanning calorimetry and dynamic mechanical analysis. Microphase separation in the synthesized PUUs was monitored using atomic force microscopy (AFM) to find a better insight into structure–property relationship of PUUs consisting of mixed polyols. Thermal analysis of the polymers revealed that by introducing poly(ethylene glycol) (PEG) in PUU backbone, a well-defined glass transition was obtained. The results of AFM showed that PCL-based poly(urethane urea) has a morphology in which hard segment domains were homogeneously distributed in the soft segment matrix. In the samples based on PCL/PEG, the hard segment domains aggregates were connected to each other and were inhomogeneously distributed in the matrix. Comparison of the overall data revealed that the differences in soft segment compositions had a marked effect on the molecular structure and the mechanical properties of PUUs.

**Keywords** Poly(urethane) urea · Phase domain · Microphase separation · Atomic force microscopy

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## Introduction

Over the last few years, segmented polyurethanes (PUs) have received considerable attention because of offering a combination of biodegradability, elastomeric properties and thermoplastic processing conditions, which make them potential candidates for novel applications, especially in tissue engineering and medical devices [1–3]. In contrast to traditional elastomers, these thermoplastic elastomers owe their unique mechanical properties to the presence of thermoreversible cross-linkages. The segmented PUs which contain alternating soft and hard segments may suggest unique possibilities of tailor-made polymers by varying block length and composition. The block with a glass transition temperature below zero is known as soft segment and it is usually a polyester or polyether and the second block is recognized as hard segment [4, 5]. The phase-separated structure and two-phase morphology in these segmented block copolymers are due to thermodynamic immiscibility between the hard and soft segments. Parameters such as volume fractions, chemical composition, molecular weight and molecular weight distribution of each segment have great influence on physically cross-linked network behavior and mechanical properties of PUs and polyureas as well as their microphase-separated structure. Therefore, the study of the degree of microphase separation between the hard and soft segments in poly(urethane urea)s (PUUs), based on mixed soft segments, plays a key role in better understanding of the mechanical behavior of PUUs.

The microphase segregation of segmented PUs has been studied by a variety of characterization techniques, including dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) [6–8], infrared spectroscopy [9, 10] and small-angle X-ray scattering