Characterization and Degradation Behavior of Segmented Poly(urethaneurea)s with Lysine-Based Diisocyanate

Various environmentally friendly biodegradable polymers have been developed. However, the majority of these polymers are typically hard and brittle plastics, and few biodegradable elastomeric polymers have been synthesized so far. The recent development of diisocyanates based on lysine has removed an obstacle to the synthesis of polyurethane elastomers, which are expected to yield non-toxic degradation products. If the lysine-based diisocyanate component in SPUU were liberated by hydrolysis of the urethane bonds of the polymer during degradation, the products would be lysine derivatives, which are essentially non-toxic products. In this study, segmented poly(urethaneurea)s (SPUU) were synthesized from lysine-based diisocyanate. To evaluate the molecular aggregation states of soft and hard segments, wide-angle X-ray diffraction (WAXD), and small-angle X-ray scattering (SAXS) were performed. The degradation behavior was investigated by a biochemical oxygen demand (BOD) test.

SPUU were synthesized via a standard two-step prepolymer method. LDI (lysine-based diisocyanate: LDI) was reacted with polycaprolactone diol (PCL) as a prepolymer reaction for 180 min at 358 K. Then, 1,4-butanediamine (BDA) was added to the prepolymer and allowed to react for 1 h in DMF. The soft segment consisted of PCL and LDI, whereas the hard segment consisted of LDI and BDA. Sample names were designated as PCL (PCL M_n) (PCL fraction)LDI-BDA. The obtained polymers were multi-block copolymers of hard and soft segments.

SPUU films were characterized by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) using a laboratory X-ray source, and small-angle X-ray scattering (SAXS) at beamline **BL40B2**. Degradation studies were performed by a BOD test in an activated sludge according to JIS K 6950, using activated sludge taken from a sewage plant in Meito-ku, Nagoya.

Differences in state of molecular aggregation of SPUU were confirmed by DSC. Crystal melting of PCL in the soft segments was observed between temperatures of 283 K and 320 K. The crystallinity of PCL decreased with a decrease in PCL content. This crystal melting of PCL did not occur in the case of PCL(1250)(71)LDI-BDA. Decreasing PCL content over 71 wt%, a baseline shift corresponding to the glass transition temperature (T_g) of the hard segments was observed between temperatures of 370 K and 380 K.

The crystallinity of the soft and hard segments was investigated by WAXD measurements. SPUU containing long soft segments showed PCL crystalline diffraction peaks at q = 15.1 (d = 0.41 nm), 15.6 nm (d = 0.40 nm), and 16.8 nm (d = 0.38 nm) corresponding to the orthorhombic (110), (111), and (200) planes, respectively. In this SPUU, these peaks became weak with a decrease in PCL content, and disappeared for PCL(1250)(71)LDI-BDA.

The phase structure of SPUU was characterized

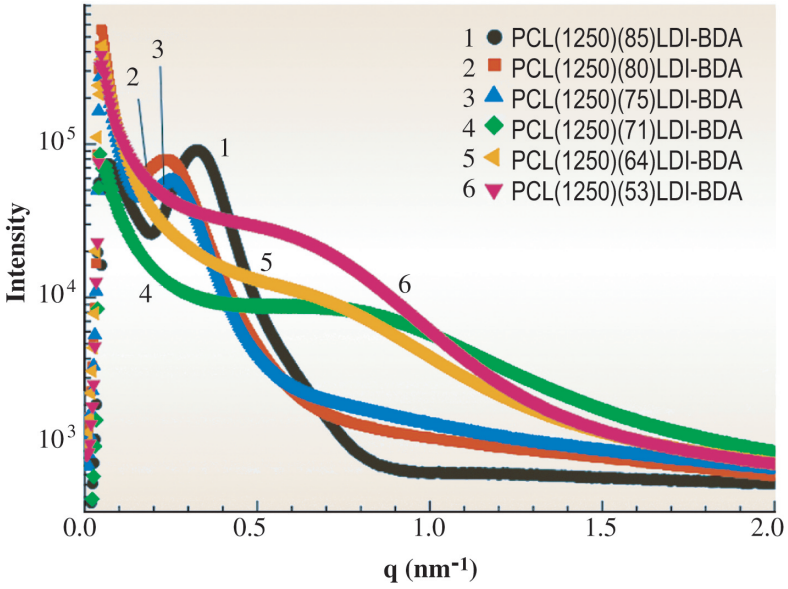

Fig. 1. The dependence of corrected intensity on scattering vector, q for PCL(1250)(X)LDI-BDA.

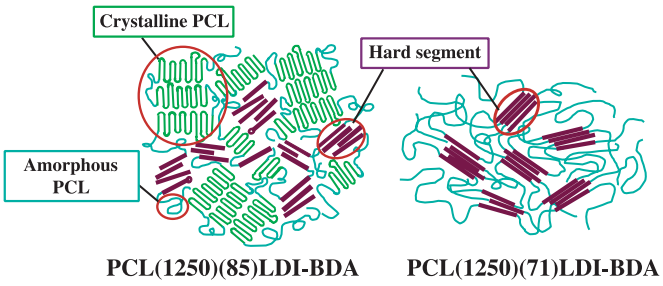

Fig. 2. The structure model of PCL(1250)(X)LDI-BDA.

by synchrotron SAXS measurements. SAXS was measured at BL40B2. Figure 1 shows the dependence of the corrected intensity on the scattering vector, q of SPUU. Here q is defined as $4\pi \sin\theta/\lambda$. The large peak observed at q = *ca.* 0.23-0.33 nm^{-1} (L = 27.3-19.6 nm) is attributed to the long period between the PCL crystallites. Even for PCL(1250)(85)LDI-BDA without the hard segment component, the long period was clearly observed. The intensity of this peak decreased with an increase in the hard segment content and disappeared for PCL(1250)(71)LDI-BDA. Also, this peak disappeared above the melting temperature of PCL. However, a scattering peak corresponding to the distance between the hard segment domains was observed in PCL(1250)(71)LDI-BDA. The structure model of PCL(1250)(X)LDI-BDA based on the above-mentioned characterization is depicted in Fig. 2. In the case of a high PCL fraction, PCL formed a stacked and folded lamellar crystal between hard segment domains. Since the PCL formed a lamellar crystal, PCL(1250)(X)LDI-BDA with X > 75 formed a three-phase structure consisting of the glassy hard segment, amorphous PCL and a crystalline PCL phase. On the other hand, in the case of PCL(1250)(X)LDI-BDA with X = < 71, a two-phase structure consisting of the hard and soft segments appeared due to the loss of crystallinity of PCL in the soft segment phase.

To investigate the biodegradability of SPUU, a BOD degradation test was carried out. The BOD degradation rate of SPUU was increased with increasing PCL content (Fig. 3). SPUU with a high PCL content (above 71 wt%) showed the high degradability in the activated sludge. On the other hand, SPUU with a low PCL content (64 wt% and 53 wt%) showed low degradability. This indicated that the ester linkages of PCL were degraded easily by microorganisms.

Biodegradable segmented poly(urethaneurea)s (SPUU) were successfully synthesized from lysine-based diisocyanete (LDI), with polycaprolactone diol (PCL) and 1,4-butanediamine (BDA) constituting the hard segments. Thermal analysis by DSC and structural analysis by SAXS and WAXD measurements revealed that the relative ratio of PCL to BDA segments in SPUU changed the crystallinity of the PCL segment and the microphase separation structure consisting of soft and hard segments.

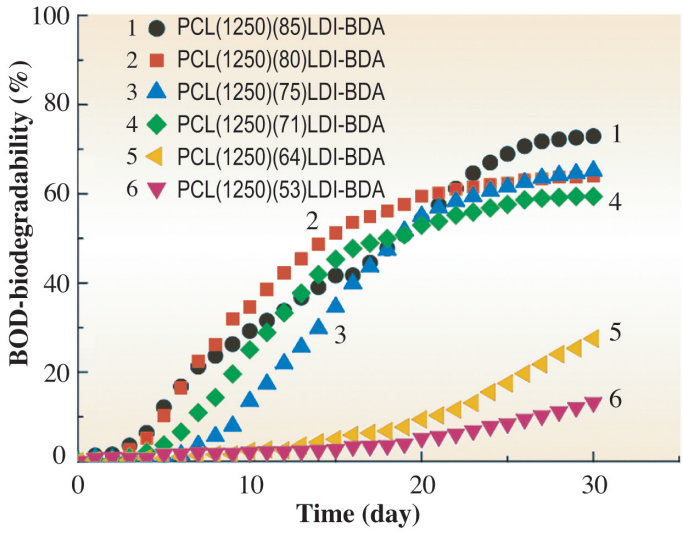

Fig. 3. The BOD degradation behaviors of PCL(1250)(X)LDI-BDA.

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