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Effect of ethanol solution of iodine on degradation of poly(ε-caprolactone)

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S1. Experimental Section

i-PCL fiber preparation

i-PCL fibers 750-780 μm in diameter were prepared from PCL granules (Sigma-Aldrich, United States) with the following parameters: molecular weight (M_w), 169 kDa; dispersity, 1.51; glass-transition temperature, -60 °C; melting temperature, 60 °C; and degree of crystallinity, 55%, by a melt technology at 100 °C in a DSM Xplore 5 ml Microcompounder (Netherlands) by extruding a polymer melt through a round die 1 mm in diameter. At the compounder outlet, the fibers were cooled with an air jet and wound on a spool of the receiving unit.

Determination of iodine content

The iodine content was determined as the weight gain of an initial fiber after the filler incorporation followed by drying to a constant weight. The samples were weighed with an AND ER182A electronic balance (accuracy of ±0.0001 g). The measurements were performed for three samples. Relative error of I_2 content measurement was 5%.

GPC investigations

The GPC curves were obtained with a Waters 510 analytical chromatograph equipped with a differential refractometer 410 and three UltraStiragel columns (10^2 and 10^4 nm, linear): tetrahydrofuran as an eluent; temperature was 35 ^oC; and flow rate was 1 ml min^{-1}. Molecular-weight characteristics were calculated relative to polystyrene standards using DataModule-730.

^1H NMR investigations

The spectra (presented in Appendix 1) were recorded with a Bruker BioSpin instrument (Germany) and a 700 MHz Varian NMR-system spectrometer VNMRS-700 (Varian-Agilent, United States) in $CDCl_3$ solutions at 30 °C.

S2. Optical micrographs of iodine-containing PCL fiber

Optical microscopic investigations were carried out with a Carl Zeiss Jena polarization microscope.

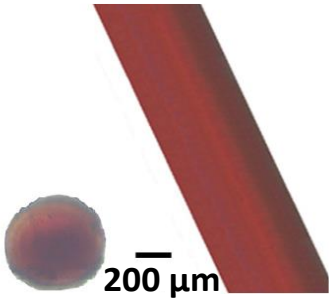

Figure S2. Optical micrographs (side view and thin transverse section) of **pI$_2$-PCL** fiber.

S3. ^{1}H NMR data

A PCL monomer unit consists of five methylene groups (-CH_2-), with each of them containing two hydrogen atoms. Two methylene groups denoted by numeral 2 have similar chemical environments; therefore their signals are overlapped in the range of the chemical shifts from 1.50 to 1.80 ppm. Three other methylene groups exhibit signals in the chemical shift ranges of 1.25-1.50, 2.15-2.45, and 3.90-4.20 ppm, respectively, because they have their own chemical environments. A more detailed analysis of the ^{1}H NMR spectra has revealed signals with much lower intensities than the intensities of the methylene groups in the polymer backbone. The signals in the chemical shift ranges of 1.70-1.90, 2.60-2.65, and 4.20-2.25 ppm are related to the methylene groups of the monomer, *i.e.*, ε-caprolactone. Since the chemical environment of protons in methylene groups located in the end monomer units (terminal groups) differs from the environment of those in the polymer backbone, they possess their own signal at chemical shift (3.65 ppm). It was hypothesized that the signals at 4.12 (quartet, 2H) and 1.25 ppm (triplet, 3H) are related to terminal ethoxycarbonyl groups –C(O)O–CH_2–CH_3, which can be formed as a result of PCL transesterification in the presence of ethanol.

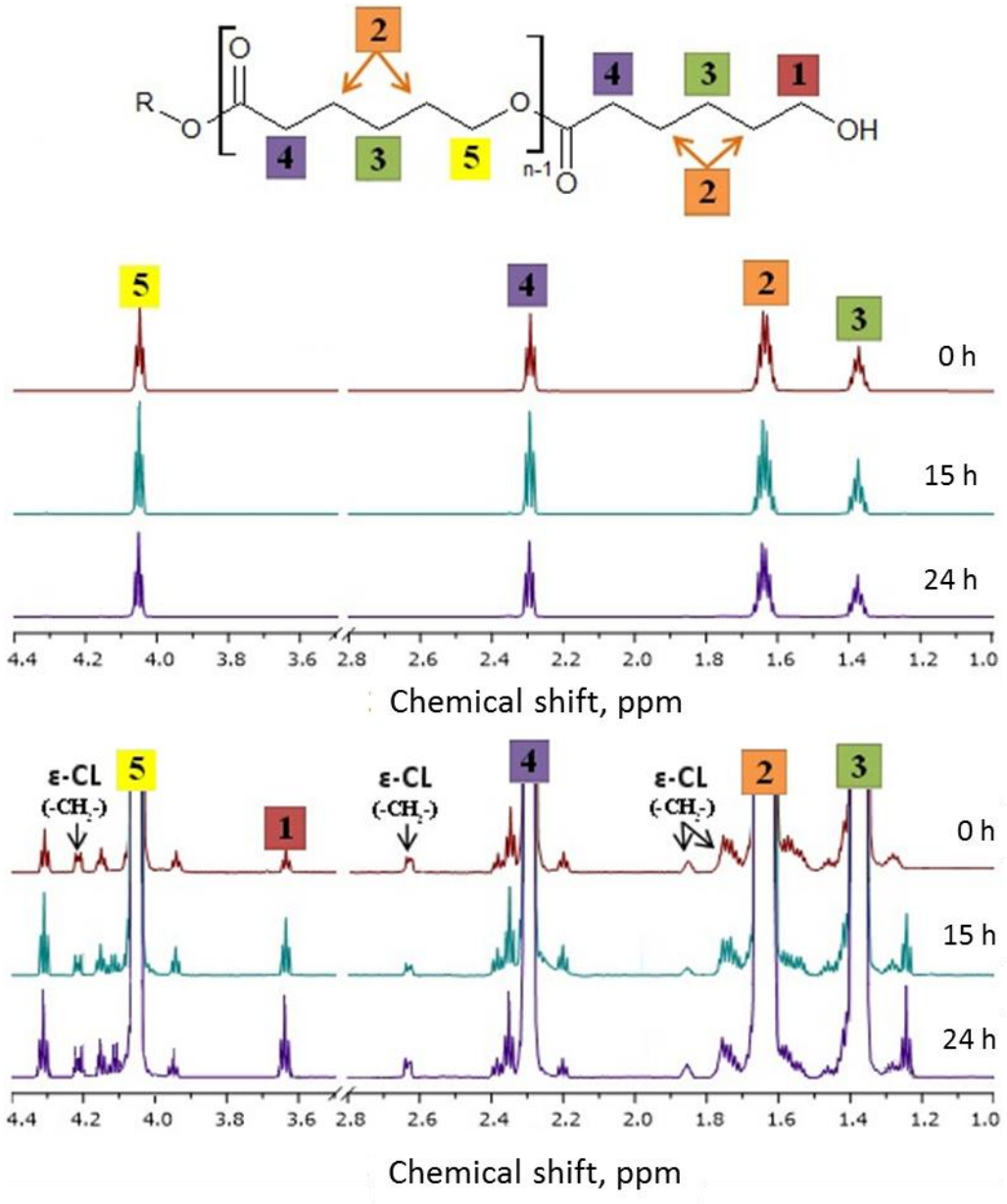

Figure S3. ^{1}H NMR spectra ($CDCl_3$) of isotropic PCL fibers exposed in a 10% water-ethanol solution of iodine for 0, 15, and 24 h.

S4. Iodine-catalyzed PCL alcoholysis reaction

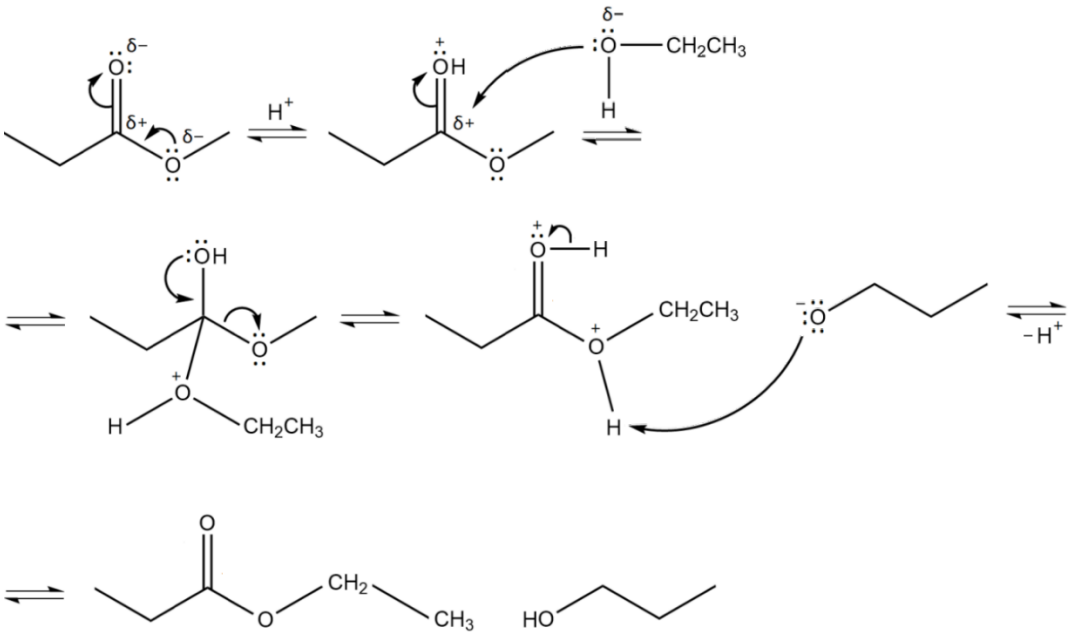

Figure S4. Mechanism of PCL transesterification (alcoholysis) under the action of ethanol in an acidic medium.

Thus, the rupture of an ester bond in the polymer chain under the action of ethanol in an acidic medium must lead to the formation of two shorter chains. One chain should contain a hydroxy terminal group (an increase in the intensity of the terminal group signal at 3.65 ppm), while another chain contains an ethoxycarbonyl terminal group.

S5. Calculation of the effective rate constant of PCL degradation *via* transesterification in the ethanol solution of iodine.

Lyu, Sparer and Untereker [*J. Polymer Sci., Part B: Polymer Physics*, 2005, **43**(4), 383, doi:10.1002/polb.20340] have proposed a model for hydrolytic degradation of, in particular, polyesters through a second-order mechanism. Three stages of degradation are distinguished in this case. At the first stage, a polymer is saturated with water. At the second stage, hydrolysis occurs; however, low-molecular-mass products are retained inside a sample. When the hydrolysis reaches the third stage, the low-molecular-mass products begin to dissolve in water.

In this work, the aforementioned model was suggested to be used for determining the effective rate constant of PCL alcoholysis under the action of ethanol and iodine in an acidic medium. This is feasible, because the sample mass remains unchanged during the period of the experiment (24 h), thus indicating that the process under consideration occurs at the second stage of degradation, when the formed low-molecular-mass reaction products are not washed away. In this case, the reciprocal number N of bonds in the polymer chain is described as a function of time t by the following equation:

$$\frac{1}{N(t)} = k \cdot C_s \cdot (t - t_i).$$

Here, $N = M_n/M_{un}$, where M_n and M_{un} are the number-average molecular mass of PCL (see main text, Table 1) and the molecular mass of a polymer unit (114 Da), respectively; C_s is the solubility of ethanol in the polymer, *i.e.*, a constant equal to 0.04 (4 wt %); and t_i is the effective induction time of bulk erosion (if the bond rupture occurs much slower than the saturation process, t_i is the time required to saturate the polymer with ethanol). This time is equal to 1 h.

Figure S5 shows the obtained $N(t\text{-}t_i)$ dependence, from which the slope of the $k \cdot C_s = 3 \cdot 10^{-4}$ h^{-1} straight line was determined. In this case, $k = 7.5 \cdot 10^{-3}$ h^{-1}.

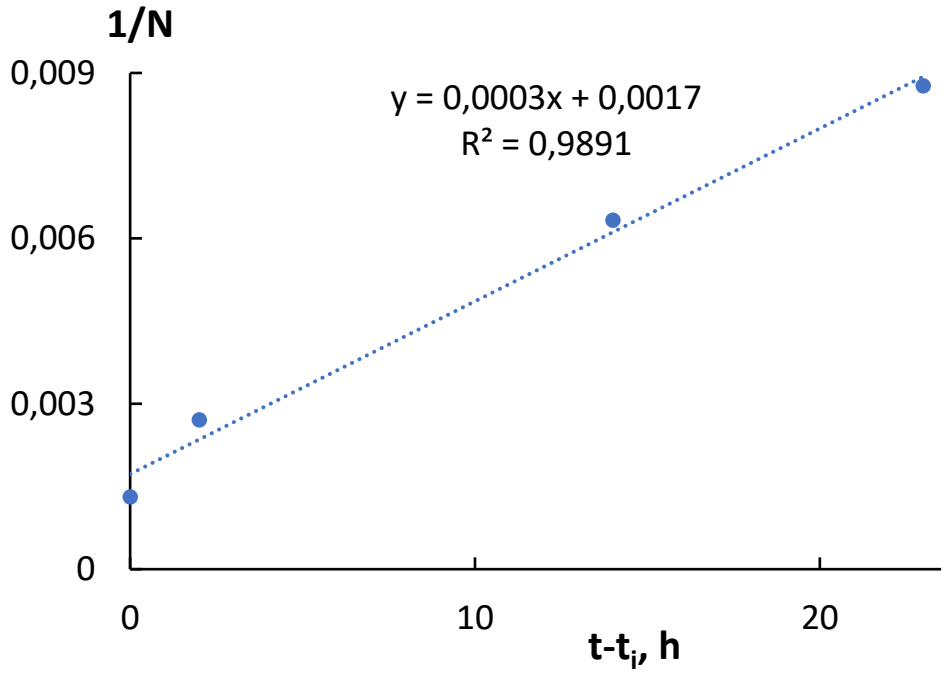

Figure S5. Dependence of the reciprocal number *N* of bonds in the polymer chain on time *t* with account of induction time t_i = 1 h approximated by a linear function.