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Polycaprolactone degradation under the action of iodine vapor

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Appendix 1. Experimental Section

Films 100 μm thick and fibers 1500 μm in diameter with a crystallinity of 50–52% were prepared from PCL granules (Sigma-Aldrich, United States) having the following initial parameters: molecular weight M_n of 112 kDa, dispersity of 1.5, glass-transition temperature of -60 °C, and metting temperature of 60 °C. The films were obtained by hot pressing followed by fast quenching in cold water, while the fibers were formed by extrusion with the use of a twin-screw DSM Xplore 5 ml Microcompounder setup (Netherlands) followed by cooling with an air jet.

Iodine content was determined as a relative gain in the mass of an initial sample after sorption. The samples were weighed with an AND ER182A electronic balance (Japan). The error in the determination of I_2 content was 5%.

The UV-Vis spectra (shown in Figure S2-1(a)) of the samples in chloroform solutions were recorded with a Cary 1E Varian instrument (United States) operating at a scanning velocity of 200 nm/min.

The Raman spectra (shown in Figure S2-1(b, c)) were recorded with a LabRAM HR Evolution spectrometer equipped with a Syncerity OE detector. Diffraction grating spacing was 1.67 μm. A laser operating at a power of 10 mW and a wavelength of 532 nm and an Olimpus MPLN10X objective were used. The data collection time was varied from 15 to 30 s.

The apparent molecular weight characteristics of PCL were determined by GPC on a Knauer chromatographic system equipped with a refractometric detector. THF was used as an eluent, whose flow rate was 1 ml/min. Chromatographic analyses were carried out at 40°C using an Agilent PLgel MIXED-C column. The calibration was performed relative to polystyrene standards.

The ^{1}H NMR spectra were recorded with a Varian VNRMS-700 instrument (700 MHz) in $CDCl_3$ used as a solvent at 30°C. The spectra were processed using the MestReNova software (Masterlab Research S.L.). The chemical shifts of the proton signals were expressed in parts per million relative to the signal of the residual nondeuterated solvent, whose chemical shift was taken to be 7.26 ppm.

An UFO-01-250N device (USSR) was used, which was equipped with a DRP 250 lamp and operated in a wavelength range of 280–400 nm. The iodine sorption process was carried out in a quartz flask. The distance between the flask and the lamp was 95 cm.

Appendix 2. Study of PCL samples by the methods of UV-Vis and Raman spectroscopy

The spectroscopic investigations have shown the formation of iodide ions as a result the interaction between PCL and I_2 vapor. Figure S2-1(a) presents the UV-Vis spectra measured for chloroform solutions of PCL before and after the treatment with iodine vapor, as well as the spectra of chloroform and an iodine solution in chloroform. The assignment of the absorption bands in the presented spectra is as follows: 270 nm, PCL; 280 and 360 nm, I^{3-} in the charge-transfer complex; 292 nm, I^{3-} solvated by the solvent; and 510 nm, I_2 in the free form.

Figures S2-1(b,c) show the Raman spectra of the initial and iodine-containing PCL films. The spectra exhibit the following absorption bands inherent in PCL: 1440 and 1414 cm^{-1}, bending vibrations (δ) of CH_2 groups in polymer backbones and near carbonyl groups, respectively; 1108 cm^{-1}, stretching symmetric vibrations (ν_s) of C–C bonds; and 912 cm^{-1}, ν_s of C–COO bonds. In addition to the bands corresponding to PCL, the low-frequency region of the spectrum for the iodine-containing sample shows bands corresponding to vibrations of bonds in various polyiodide ions. The interpretation of these bands is given in Table S2-1.

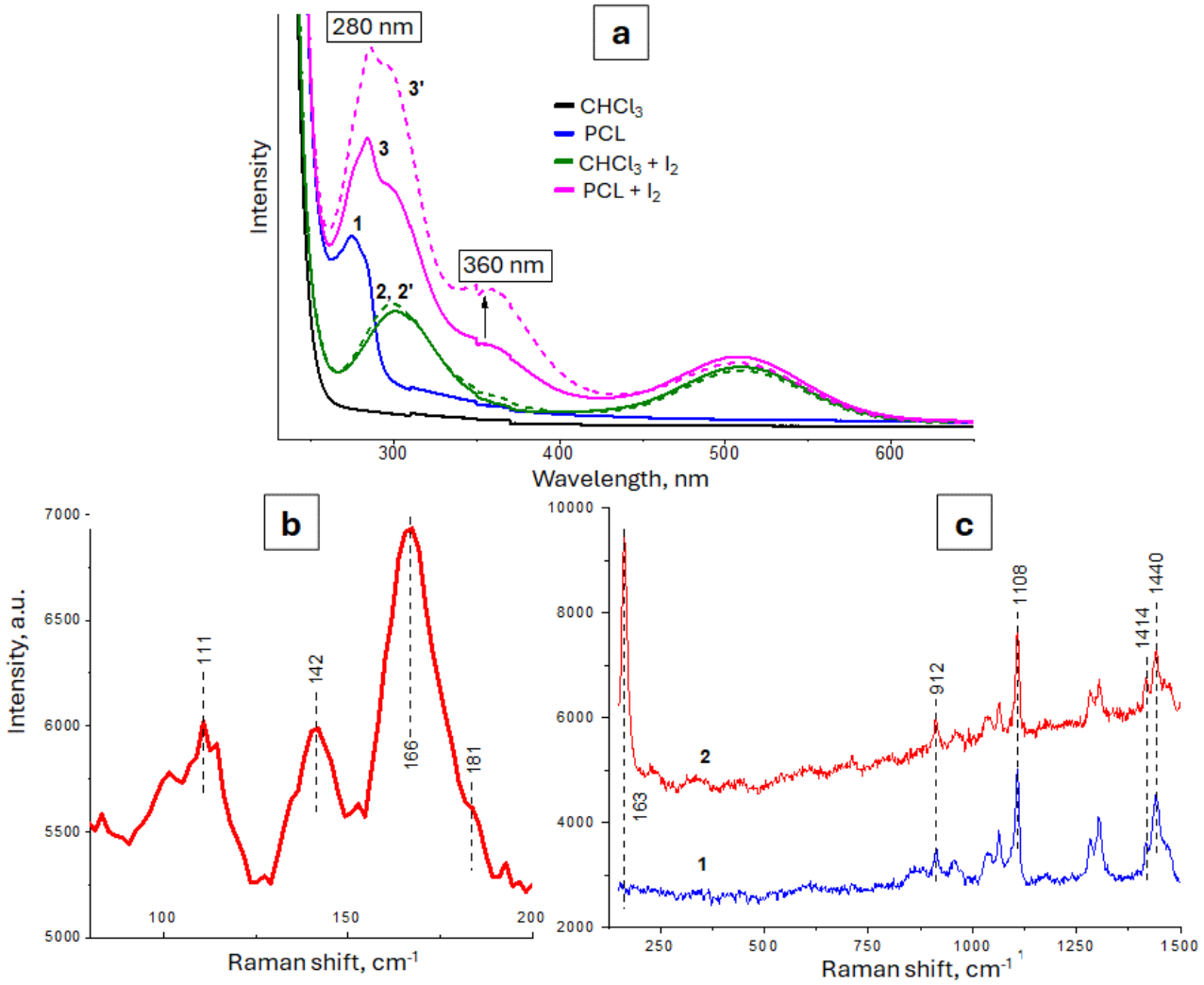
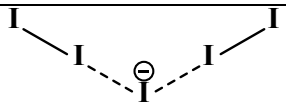
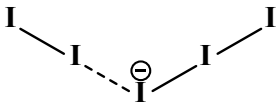


Figure S2-1. (a) UV-Vis spectra for solutions of (1) PCL, (2,2') iodine, and (3,3') PCL with iodine in chloroform obtained immediately (solid lines) and in 24 h; (b) Raman spectrum measured in a range of 10–200 cm^{-1} for a PCL film exposed in iodine vapor; and (c) Raman spectra measured in a range of 150–1500 cm^{-1} for (1) initial PCL film and (2) the film exposed in iodine vapor.

Table S2-1. Assignment of the bands in the Raman spectrum within a range of 10–200 cm^{-1} for an iodine-containing PCL film

Ion structure	I_n	Vibration mode	Raman shift, cm^{-1}
 Symmetric linear	I_3^-	ν_s	111
 Asymmetric linear	I_3^-	ν_{as}	142
 V-shaped $[(I^-) \cdot 2I_2]$	I_5^-	ν_s	167 111
 L-shaped $[(I_3^-) \cdot I_2]$	I_5^-	ν_s ν_{as} ν_s	167 142 111

Appendix 3. Gel-permeation chromatography data

Figure S3-1 presents molecular-weight distribution (MWD) curves for PCL film samples exposed in iodine vapor under different conditions for (a) 5 h and (b) longer time periods.

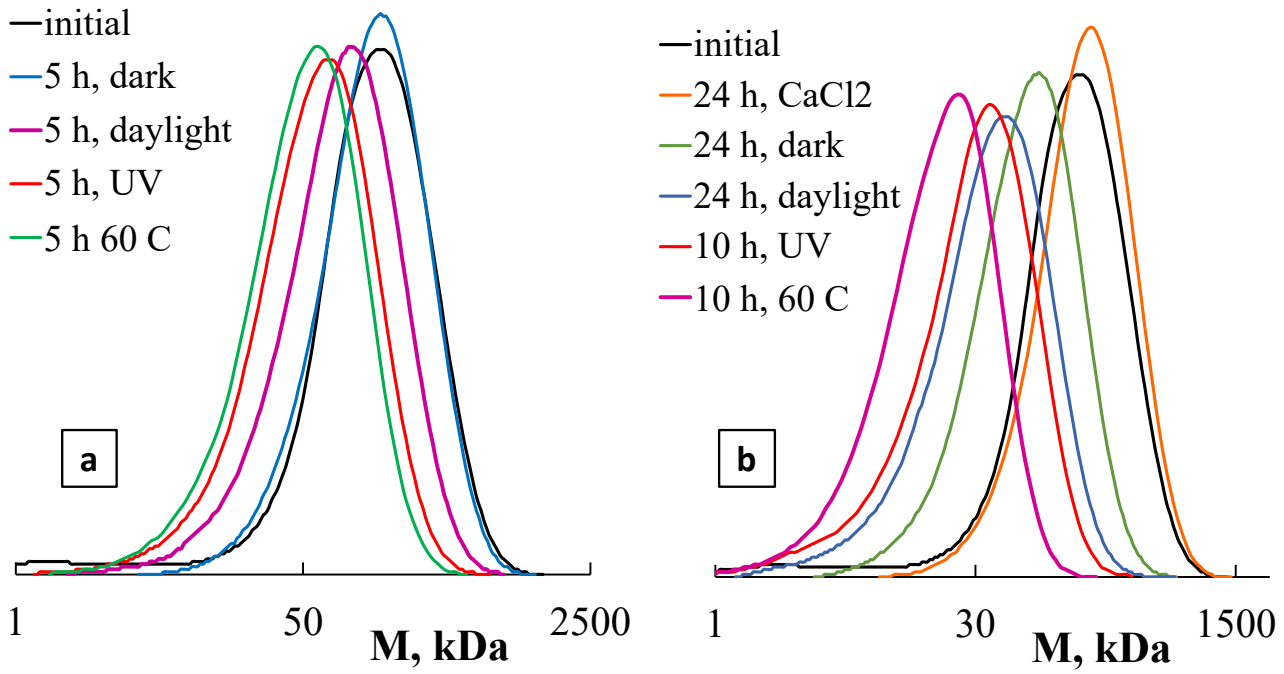


Figure S3-1. MWD curves for PCL samples exposed in iodine vapor under different conditions for (a) 5 h and (b) longer time periods.

Appendix 4. ^{1}H NMR data

Figure S4-1 shows ^{1}H NMR spectra of an initial PCL film, and the films exposed in iodine vapor with heating to 60°C and under UV irradiation.

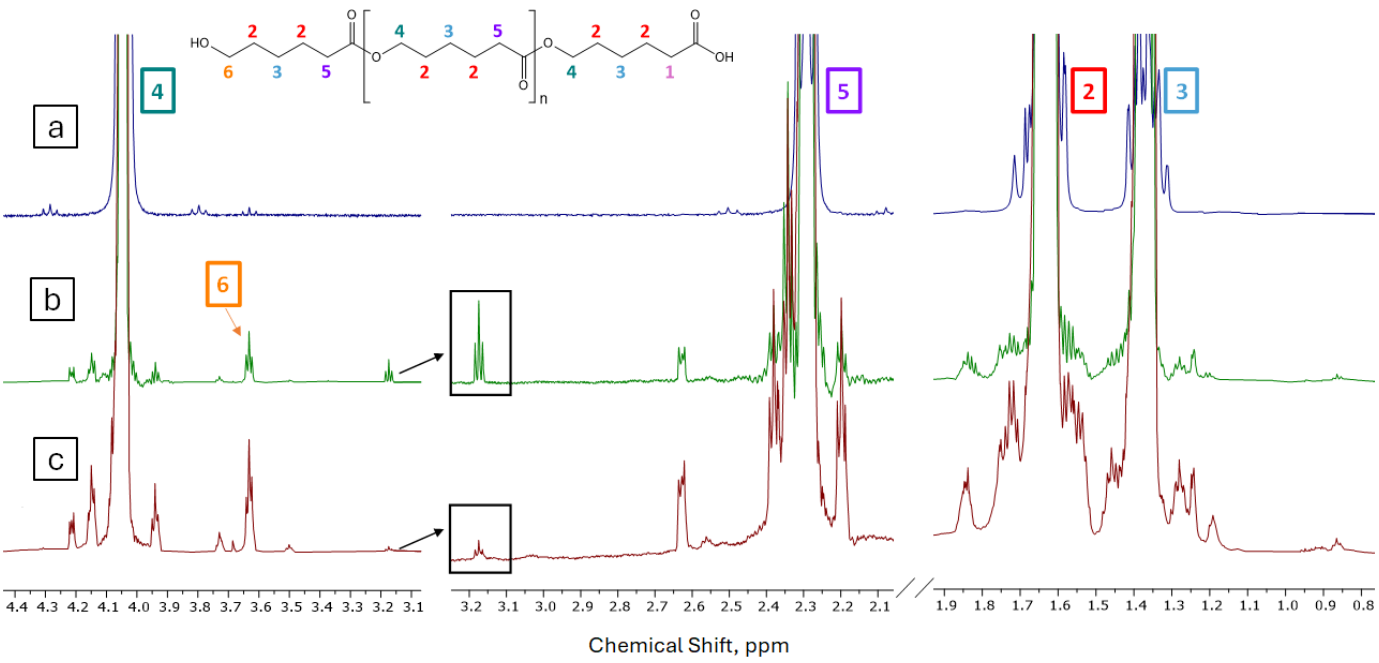


Figure S4-1. ^{1}H NMR spectra ($CDCl_3$) of (a) initial PCL film and films exposed in iodine vapor (b) at 60°C for 10 h and (c) under UV irradiation for 13 h.

The chemical shifts of proton signals are presented in parts per million (ppm) relative to the signal of the residual nondeuterated solvent, whose chemical shift was taken to be 7.26 ppm. ε-CL is ε-caprolactone.

For pure PCL: ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 4.04 (t, C**H**$_2$O), 3.63 (t, C**H**$_2$OH), 2.29 (t, C**H**$_2$CO$_2$), 1.58–1.72 (m, C**H**$_2$CH$_2$CO$_2$H), 1.31-1.42 (m, C**H**$_2$CH$_2$CH$_2$CO$_2$H).

For an iodine-containing PCL film obtained under UV irradiation for 13 h: ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 4.19 (t, C**H**$_2$O in ε-CL), 4.03 (t, C**H**$_2$O), 3.62 (t, C**H**$_2$OH), 3.16 (t, C**H**$_2$I), 2.61 (t, C**H**$_2$C(O) in ε-CL), 2.32 (t, C**H**$_2$CO$_2$H), 2.27 (t, C**H**$_2$CO$_2$), 1.82 (tt, C**H**$_2$CH$_2$I), 1.49–1.78 (m, C**H**$_2$CH$_2$CO$_2$H), 1.30-1.41 (m, C**H**$_2$CH$_2$CH$_2$CO$_2$H), 0.85 (t, C**H**$_3$CH$_2$).

For an iodine-containing PCL film obtained with heating to 60°C for 10 h: ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 4.20 (t, C**H**$_2$O in ε-CL), 4.03 (t, C**H**$_2$O), 3.61 (t, C**H**$_2$OH), 3.16 (t, C**H**$_2$I), 2.60 (t, C**H**$_2$CO$_2$ in ε-CL), 2.32 (t, C**H**$_2$CO$_2$H), 2.27 (t, C**H**$_2$CO$_2$), 1.82 (tt, C**H**$_2$CH$_2$I), 1.49–1.77 (m, C**H**$_2$CH$_2$CO$_2$H), 1.30-1.41 (m, C**H**$_2$CH$_2$CH$_2$CO$_2$H), 0.84 (t, C**H**$_3$CH$_2$).

When analyzing the degradation of polymers by the method of proton magnetic resonance, one may encounter a number of difficulties, including the low intensity of the signals from terminal groups, as well as their partial or complete overlapping with signals due to other protons of a polymer chain. It has been found that, during degradation, in parallel with an increase in the integral signal intensity of terminal methylene protons (6), triplet (1) with a comparable intensity arises at 2.35 ppm in the ^{1}H NMR spectra. It is known from the literature data that this signal may be attributed to

methylene protons adjacent to terminal carboxyl groups in PCL chains. In order to confirm the origin of this triplet, an additional experiment was performed with the introduction of a strong acylating agent, trifluoroacetic anhydride (TFAA), into an NMR tube. When measuring the spectrum, TFAA was added to the tube in an amount of 2–3 μl. Figure S4-2 presents the ^{1}H NMR spectra measured for a PCL sample exposed in iodine vapor at 60°C for 10 h in the initial mode and after acylation with TFAA. It is seen that, after the interaction of the terminal groups with trifluoroacetic anhydride, the studied signals attributed to the neighboring methylene hydrogen atoms are completely shifted to the weak-field region: at the hydroxyl group, from 3.61 to 4.34 ppm, and at the carboxyl group, from 2.32 to 2.63 ppm. The data obtained lead us to assume that signal "1" of the spectrum in Fig. S4-1 is indeed due to the terminal methylene protons adjacent to the carboxyl groups that arise as a result of the cleavage of ester bonds in iodine vapor at 60°C.

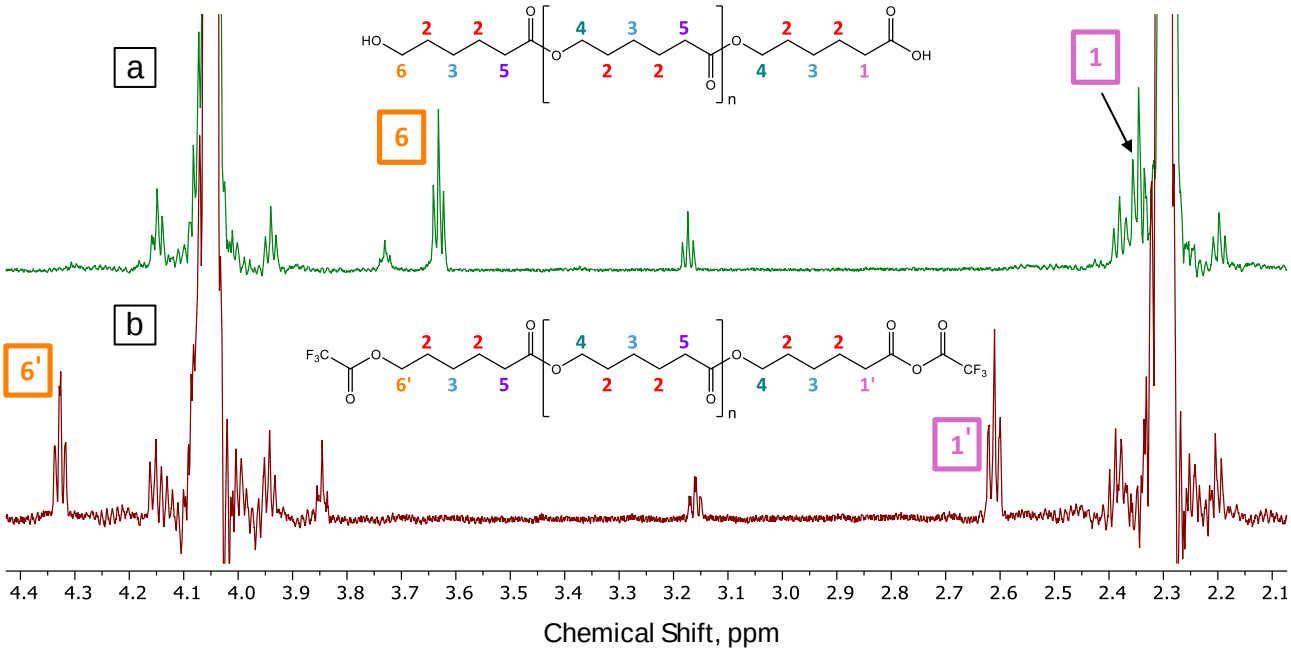


Figure S4-2. ^{1}H NMR spectra ($CDCl_3$) measured for a PCL sample exposed in iodine vapor at 60°C for 10 h (a) before and (b) after treating with TFAA.

The complete interpretation of the spectrum of the iodine-containing PCL film obtained with heating to 60°C for 10 h and treated with TFAA (the chemical shifts along the δ scale are presented in parts per million relative to Me_4Si used as an internal reference): ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 4.34 (t, C**H**$_2$OH/C**H**$_2$OC(O)CF_3), 4.07 (t, C**H**$_2$O), 3.18 (t, C**H**$_2$I), 2.63 (t, C**H**$_2$$CO_2$H/C**H**$_2$$CO_2$C(O)$CF_3$), 2.31 (t, C**H**$_2$$CO_2$), 1.92 (tt, C**H**$_2$$CH_2$I), 1.58–1.70 (m, C**H**$_2$$CH_2$$CO_2$H), 1.32-1.45 (m, C**H**$_2$$CH_2$$CH_2$$CO_2$H).