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Polycaprolactone degradation under the action of iodine vapor

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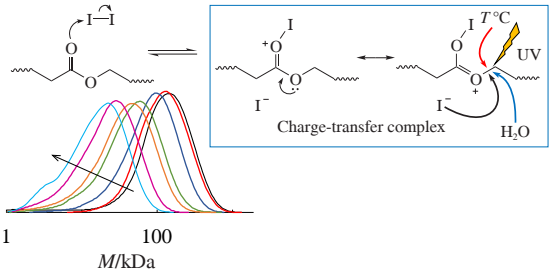
Upon the solid-state degradation of poly(ε-caprolactone) under the action of iodine vapor, the number-average molecular weight of the polymer decreased by almost an order of magnitude 48 h after the incorporation of iodine (~6 wt%) from a gaseous phase. A polymer degradation mechanism through the cleavage of C–O bonds in the polymer backbones with the formation of a charge-transfer complex involving water or polyiodide ions was proposed.



Keywords: poly(ε-caprolactone), iodine, degradation, charge-transfer complex, polyiodide ions.

Biodegradable polymers are being increasingly applied in medicine (suture materials, implants, drug delivery systems, *etc.*), agriculture (agrofilms, pots for seedings, *etc.*), 3D printing, and production of packaging materials.[1] Among synthetic biodegradable polymers, aliphatic polyesters such as polyglycolide, polylactide, poly(ε-caprolactone) (PCL), and their copolymers are prevailing;[2] they are good bases for biomedical items.[3] However, the widely spread application of these materials is often complicated by their long-term degradation. To overcome this limitation and improve the properties of the polymers, they are targetedly modified by varying their molecular weight, chemical structure, and morphology and by incorporating various fillers.[4,5]

PCL is characterized by good mechanical properties, ease of processing and molding, biocompatibility, bioresorbability, and shape memory. Therefore, the development of PCL-based functional materials with controlled degradation profile is of undoubted interest.[6,7] As found previously, the incorporation of iodine from water–alcohol solutions into polylactide fibers markedly accelerated their hydrolytic degradation,[8] while the degradation of PCL *via* alcoholysis was substantially accelerated in an alcohol solution of iodine.[9] However, the presence of a liquid had a substantial effect on the cleavage of the ester bonds.

The goal of this work was to study the degradation of solid poly(ε-caprolactone) films and fibers under the action of molecular iodine vapor to understand the mechanisms involved in this process.

Isotropic PCL films and fibers† were used as the test materials. Molding did not affect significantly the molecular-weight characteristics of the samples. The kinetics of iodine vapor sorption and desorption by the PCL films and fibers was investigated under room conditions [22–24 °C, atmospheric pressure (Figure 1)]. For this purpose, the polymer samples were placed into closed vessels over iodine granules and periodically weighed.† As a result of sublimation, the polymer sorbed iodine vapor and became colored, and the color depended on exposure time. Note that the curves of iodine sorption–desorption were similar for the film and fiber samples. The sample color intensity regularly increased with exposure time (Figure 1, insets), and the polymer acquired a dark brown color after 18 h. Figure 1 shows that the iodine content increased with time to reach a maximum in approximately 5 h. Then, the weight growth gradually decelerated. The ultimate saturation of PCL with iodine from a gaseous phase was reached in 18 h and amounted to 5.2 wt%, thus correlating with published data.[9]

Desorption of iodine from PCL has started almost immediately after the polymer samples were removed from the vessels with iodine under room conditions. Initially, the sample weight decreased drastically and reached a constant value in 19 h (Figure 1, curve *2*). Thereafter, I_2 was not completely desorbed from PCL and nearly 1.4 wt% iodine was retained in a yellowish orange polymer. Even the vacuum drying of an iodine-containing PCL sample did not lead to complete removal of I_2 and its content remained at a level of 1 wt%.

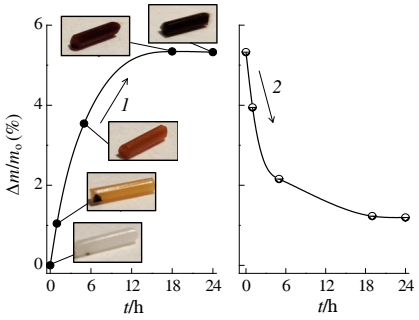


Figure 1 Curves for (*1*) sorption and (*2*) desorption of iodine by a PCL film. The insets show the photographs of PCL fiber samples exposed to iodine vapor for different time periods.

† See details in Online Supplementary Materials.

The results allowed us to assume the formation of specific bonds between iodine and the polymer, as those in complex compounds. Previously,[10] it was proposed that a charge-transfer complex (CTC) between iodine and the polyester poly(ethylene terephthalate) was formed. To confirm this assumption, we studied the iodine-containing PCL samples by UV–Vis and Raman spectroscopy.† The UV spectrum of a PCL solution in chloroform showed an absorption peak at 270 nm.[11] The addition of iodine led to the appearance of an absorption band at 280 nm and a shoulder at 360 nm, which were attributed to I_3^- ions contained in a CTC,[12] and a peak at 510 nm was assigned to free molecular I_2. The growth of the peak intensity at 280 nm and the appearance of a more distinct peak at 360 nm 24 h later indicated that the complex was not formed at once, and its concentration increased with time. The presence of iodide anions in a solid phase (in a polymer film) was proven by Raman spectroscopy. In the low-frequency region, intense bands were observed at 166, 142, and 111 cm^{-1}, which were attributed to the vibrations of bonds in various polyiodide ions.[13] Thus, the spectral data indicated that molecular iodine can interact with the functional groups of PCL even in a solid phase with the formation of a CTC.

Gel-permeation chromatography (GPC)† was used to determine molecular-weight distribution (MWD) curves for the samples. As the exposure time of PCL in iodine vapor under room conditions (temperature, 22–24 °C; relative humidity, 40–45%; daylight) was increased, the curves shifted toward lower molecular weights (Figure 2); that is, the M_n gradually decreased to 10 kDa during the experiment. At the same time, the unimodal MWD remained preserved throughout the period of degradation, while the dispersity increased by a factor of nearly 1.5. This finding indicates that that the diffusion of iodine vapor into the material was not a limiting stage of the process, while the degradation occurred in the entire polymer bulk, and it was most probably characterized by the random rupture of chains. Note that the main differences in the ^{1}H NMR spectra† of PCL before and after the treatment with iodine vapor for 24 h consisted in an increase in signals due to the terminal groups, as in the case of hydrolytic degradation. These data were used to estimate the M_n values of the polymer as the integral intensity ratio between the signals due to the methylene groups and the terminal groups of PCL. The found values of M_n were about 9 kDa.

To determine the mechanisms of iodine–PCL interactions, the process was performed under different conditions: at changed temperature (to 60 °C), humidity (over $CaCl_2$ as a desiccant), and illumination (in the dark and under a UV lamp†). Table 1 summarizes the molecular-weight characteristics of the PCL samples treated with iodine vapor.† The exposure of the polymer under the above conditions in the absence of iodine did not lead to essential changes in its molecular weight. The polymer degradation process was markedly accelerated at a temperature

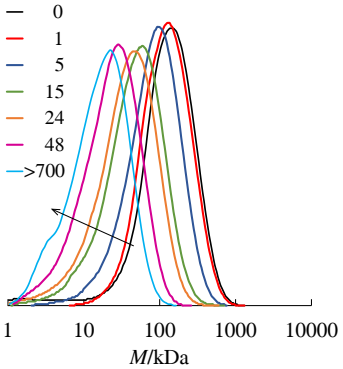


Figure 2 MWD curves for PCL samples exposed in iodine vapor for different times (the exposure times in hours refer to the corresponding curves). The arrow indicates the direction of increasing exposure time.

Table 1 Characteristics of PCL samples exposed in iodine vapor under different conditions.

Conditions	*t*/h	$\Delta m/m_o$ (%)	M_n/kDa	$Đ_M$
Room conditions	5	3.5	55	2.0
	24	5.2	22	2.3
UV irradiation	5	–	38	2.0
	13	4.1	21	2.1
In the dark	5	3.1	95	1.7
	24	4.4	44	1.9
Over $CaCl_2$	24	4.3	115	1.7
	700	–	16	2.4
Over $CaCl_2$ in the dark	288	7.8	14	2.9
Heating to 60 °C	5	6.0	34	1.9
	10	8.5	11	2.1

of 60 °C and under UV irradiation. At the same time, the degradation was markedly decelerated when the process was performed in the dark and in a dry atmosphere (over $CaCl_2$). However, even under these unfavorable conditions, the PCI still degraded, but essential changes in its molecular-weight characteristics were observed after longer processing times of about 300 h.

To find a mechanism for the rupture of backbone polymer chains under the action of iodine, the degradation products of the samples that exhibited the greatest changes in molecular-weight characteristics were studied by ^{1}H NMR spectroscopy.† The ^{1}H NMR spectra of the samples exhibited signals at 2.6 and 4.2 ppm attributed to the methylene hydrogen atoms in the ε-caprolactone monomer at carboxyl carbon atoms and alkoxyl oxygen atoms, respectively. These signals indicated the occurrence of the PCL depolymerization reaction in the presence of iodine under heating and UV irradiation. Moreover, a signal with a chemical shift of 3.16–3.18 ppm, which could correspond to the methylene terminal groups at iodine atoms, was detected. We assumed that PCL degradation was accompanied by the cleavage of C–O bonds in the backbone polymer chain with the formation of iodoalkyl groups.

Therefore, we proposed the following mechanism for PCL degradation accompanied by the rupture of the backbone polymer chain. At the first stage, a CTC was formed to weaken C–O bonds in the polymer chain (Figure 3). The occurrence of such complexes with amide bonds of nylons was considered previously.[14,15]

Then, these C–O bonds were attacked by water molecules (in trace amounts) under standard room conditions with the formation of terminal hydroxyl and carboxyl groups (reaction I in Figure 4). As a result, reaction products were formed as in hydrolytic degradation.

Under dry atmospheric conditions, iodine ions can cause chain cleavage according to mechanism II in Figure 4. The intermediate compound containing an I–O bond is unstable, and it can easily decompose under the influence of water when the sample was moved from a dry atmosphere to room conditions. When the degradation was implemented at 60 °C or under UV

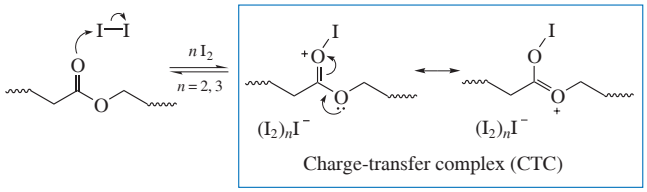


Figure 3 Mechanism of the formation of a charge-transfer complex between PCL and iodine.

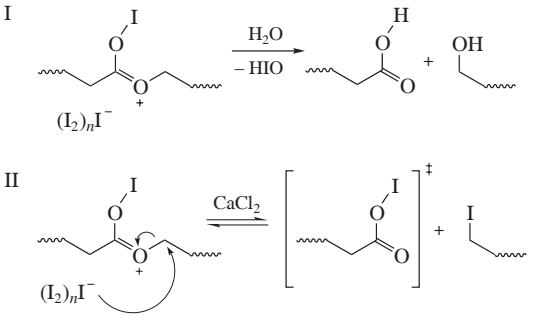


Figure 4 Mechanisms of PCL chain rupture upon interaction with iodine (I) in the presence of trace amounts of water and (II) in a dry atmosphere.

irradiation, the spontaneous heterolytic cleavage of weak C–O bonds was also possible.

Thus, the data obtained in this work are of importance both for determining the degradation mechanisms of polycaprolactone and other biodegradable polyesters under the action of molecular iodine and for solving a problem of the development of new functional materials with predictable and controllable degradation profile.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7589.

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