

Radiation-Induced Effects in Gamma-Irradiated PLLA and PCL at Ambient and Dry Ice Temperatures

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ABSTRACT: The effect of γ -rays sterilization at ambient (23°C) and at dry ice temperatures (−78°C) on two biodegradable semicrystalline polyesters, namely poly(L-lactide) (PLLA) and poly(ϵ -caprolactone) (PCL), was studied. The radical processes generated by irradiation were investigated by electron paramagnetic resonance (EPR) spectroscopy, whereas postradiation changes were monitored for 5 months by scanning calorimetry, thermogravimetric analysis, and apparent viscosity measurements. It was confirmed that the radiation sterilization initiates degradation in both studied polymers, however, the effect is smaller in PCL than in PLLA, and that the range of changes might be limited by lowering temperature of the exposure to γ -rays. Newly formed oxygen containing functional groups confirmed by EPR and

thermogravimetric analysis methods are produced in the irradiated polyesters. In PCL, the process might give rise to thermally induced cross-linking via oxygen containing intermolecular bridges. During storage, in both irradiated materials, morphology determined by differential scanning calorimetry is changing - PCL ability toward crystallization decreases insignificantly, whereas in PLLA the tendency is opposite - on irradiation a contribution of crystalline phase is growing considerably, from 18 and 19% to 41 and 31% for PLLA irradiated at 23°C and at −78°C, respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 375–383, 2011

Key words: ESR/EPR; polyesters; degradation; thermal properties; irradiation

INTRODUCTION

The interest regarding effects of ionizing radiation (γ -rays or electron beam) on some polyesters is increasing world-wide due to growing market for biodegradable polymeric biomaterials. With reference to medical devices, radiation processing is one of the method applied either to induce desirable functionality of the materials or to sterilize final products.^{1–4} Second process that results in elimination of microbial bioburdens must not trigger the deterioration of mechanical and thermal properties of the materials or diminish their stability during aging. Therefore, it is necessary to follow all alternations in radiation sterilized products and to estimate their features with time.

Poly(ϵ -caprolactone) (PCL) and poly(L-lactide) (PLLA) have attracted attention recently as biodegradable materials that might be utilized in variety of current and emerging applications, e.g., resorp-

tionable sutures, long or short term implantable devices, microparticles for drug delivery systems, bone graft substitutes, etc. Unfortunately, the mechanical properties and processability of the polyesters are poor, furthermore radiation sterilization might induce additional risk of their deterioration.^{5,6}

Aforementioned polyesters might exist either in amorphous or in crystalline forms depending on their thermal history and stereo-chemical configuration, in a case of PLA. It is well known that polymer crystallinity influences significantly mechanical properties such as yield stress, elastic modulus and impact resistance. In addition, proportion between relatively mobile amorphous phase and rigid crystalline regions is usually one of the most important factors determining radiation-induced processes.

High energy irradiation of polymers results, as a rule, in radical processes that eventually lead to degradation and/or cross-linking⁷. Radiation-induced cross-linking of polyesters is usually very limited and depends on the chemical structure as well as on morphology of the materials, and usually requires high doses. For instance, in irradiated PCL gel fraction was not found below 150 kGy.⁸ On the other hand, PCL irradiated in molten or in supercooled state (at 45°C after melting at 80°C) undergoes cross-linking just at 40 kGy due to an increasing content of amorphous phase and chain mobility.⁸ Yield of

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the process might be also enhanced by some chemical agents, usually multifunctional monomers, e.g., trimethylol propane trimethacrylate or triacrylate monomers and others.^{9,10} In the same way, some properties of PLLA could be significantly improved if only the irradiated polyester is doped with appropriate cross-linking initiators, such as triallyl isocyanurate, trimethylol isocyanurate, and trimethylol propane trimethacrylate.¹¹

Nevertheless, the predominant effect induced by γ -radiation in polyesters is supposed to be chain scission leading to a loss of tensile strength and an enhanced hydrolysis rate in the presence of aqueous medium. There are several factors that reduce an extend of the degradation in polyesters. Results published by Aliev et al.¹² and Hill et al.¹³ revealed that the efficiency of radiation degradation is restricted in aromatic polyesters and that the final effect depends on their chemical structure. Radiation stability enhances when length of a hydrocarbon linkage between ester groups increases. Thus, PBT (poly(1,4-butylene terephthalate)) is more radiation resistant than PET (poly(ethylene terephthalate)).¹² In this context, PLLA ought to be specially sensitive toward ionizing radiation due to only one methylene group that separates the ester units as well as the presence of a tertiary carbon atom in the main chain. This fact was confirmed by Nugroho et al.¹⁴ for doses in the range from 0 to 1000 kGy. Contrary to Kantoglu et al.¹⁵ who postulated random main chain damages for doses in the range of 0–80 kGy, the authors suggested that at doses up to 30 kGy chain scissions occur only in amorphous phase and crystalline regions remain unchanged.

One of the most important factors determining final effect of irradiation is temperature of the exposure, especially to γ -rays. Many bulk medical objects have to be radiation sterilized in Co-60 sources due to insufficient penetration of electron beam generated in accelerators or unacceptable inhomogeneity of the absorbed dose. On the other hand, due to low dose rates of γ -sources, the exposure time is long and the possibility of degradation increases significantly in comparison with electron beam irradiation, especially when access of air to a radiation chamber is unrestricted. The extend of polymer decomposition might be inhibited by lowering temperature of radiation exposure since under such conditions radical processes are usually suppressed.

In this study, an influence of temperature on effects induced by γ -rays sterilization in two semicrystalline polyesters, PCL, and PLLA was investigated. The changes were monitored for 5 months. Some intermediates generated during the process were identified by electron paramagnetic resonance (EPR) spectroscopy. An evaluation of radiation-induced effects requires information on the structure

of studied materials thus the temperatures and enthalpies of phase transitions, and subsequently evolution of crystallinity, were determined with the course of time using thermal analysis. The extend of degradation was evaluated by the apparent viscosity measurements that are known as a sensitive tool monitoring thermoplastic decomposition. Changes of the polyester surfaces were studied by dynamic contact angle measurements.

EXPERIMENTAL

Samples preparation and irradiation

Two semicrystalline polyesters, PLLA (Biomer 160 kDa) and PCL (CAPA 6500), were studied.

The samples were hot-pressed at 120°C (PCL) or at 220°C (PLLA) for 3 min followed by cold-pressing at ambient temperature to form the sheets with a thickness of 0.2 mm.

The polymer samples were irradiated in a Co-60 source (Issledovatel) with a dose rate of 0.96 kGy/h in air atmosphere to a dose of 25 kGy either at ambient (23°C) or at dry ice temperature (−78°C). The samples were kept for months in the dark at 23°C and successively investigated.

EPR spectroscopy

EPR spectra were recorded directly on irradiation using a Bruker ESP 300 spectrometer with a rectangular cavity TE102 at the following parameters: modulation amplitude - 0.09 mT, time constant - 80 ms, conversion time - 80 ms, microwave power - 1 mW (if not reported otherwise). The EPR spectra were detected either at ambient or a liquid nitrogen temperature (−198°C) upon annealing of the samples to temperatures indicated on Figures 1(A) and 2(A). To perform EPR measurements under cryogenic conditions, the samples on irradiation at −78°C were immediately inserted into liquid nitrogen and afterwards heated gradually before examination to the temperatures controlled by a thermocouple. The relative radical concentration was estimated by comparison of the spectral areas measured by double integration of the experimental EPR signals.

Differential scanning calorimetry (DSC)

DSC measurements were carried out using a TA Instruments differential scanning calorimeter (MDSC 2920) at a heating/cooling rate of 10 deg/min under nitrogen atmosphere at a purge rate of 100 mL/min. The temperature was calibrated using the melting point of high purity indium metal. The crystallization and melting behaviors of the polyesters were

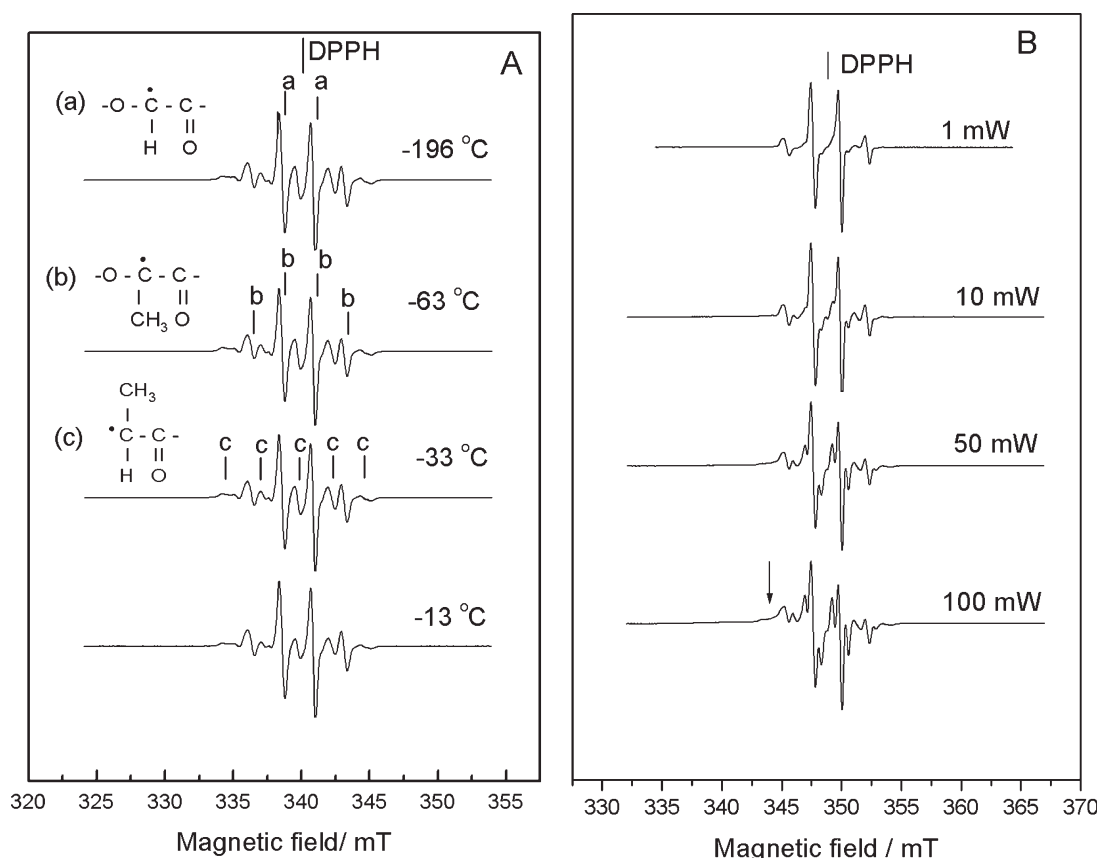


Figure 1 EPR spectra of PLLA irradiated by γ -rays to a dose of 25 kGy (A) at -78°C (spectra were detected at liquid nitrogen temperature upon annealing to the indicated temperatures) and (B) at 23°C (spectra for various microwave powers were measured at ambient temperature).

studied after erasing the thermal and mechanical history of the samples, i.e., during the second run.

Measurements were performed in the temperature range from -50 to 200°C or to 150°C , for PLLA and PCL, respectively. About 5 mg of the sample inserted in a pan was heated and cooled gradually. Afterwards, the second run was performed applying the same conditions as for the first cycle. It was assumed that the enthalpy of fusion obtained by the integration of melting transition peak is proportional to the content of crystalline regions. The reported enthalpy of fusion (135.2 J/g) was used as a reference for 100% crystalline PCL.¹⁶ Melting enthalpy of 100% crystalline PLLA was found in literature as 91.0 J/g .¹⁷

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed on a TA Instruments TGA Q500 apparatus in the range of temperature from 30 to 600°C under nitrogen atmosphere.

Rheological measurements

Apparent viscosity was measured with a CAP 2000+H Brookfield viscometer at temperatures indicated on Figure 7(A, B). Reported relationships were

obtained on the basis of five parallel measurements; average values of viscosity were calculated for each recorded point.

Dynamic contact angle measurements

Applying Wilhelmy method dynamic contact angle was studied using a Tensiometer K100C (Krüss) supplied with the thermostatable sample vessel at 25°C . Six parallel measurements were performed for each sample.

RESULTS AND DISCUSSION

Radical processes

Radiation-induced radicals are responsible for physicochemical changes in the studied polyesters thus in the first stage of investigations the nature of intermediates as well as kinetics of their decay were determined.

Figure 1(A) shows a sequence of the experimental EPR spectra of PLLA recorded at liquid nitrogen temperature, i.e., at -198°C , upon γ -irradiation at -78°C and following annealing to the indicated temperatures. The samples were inserted into liquid nitrogen to stabilize generated during irradiation

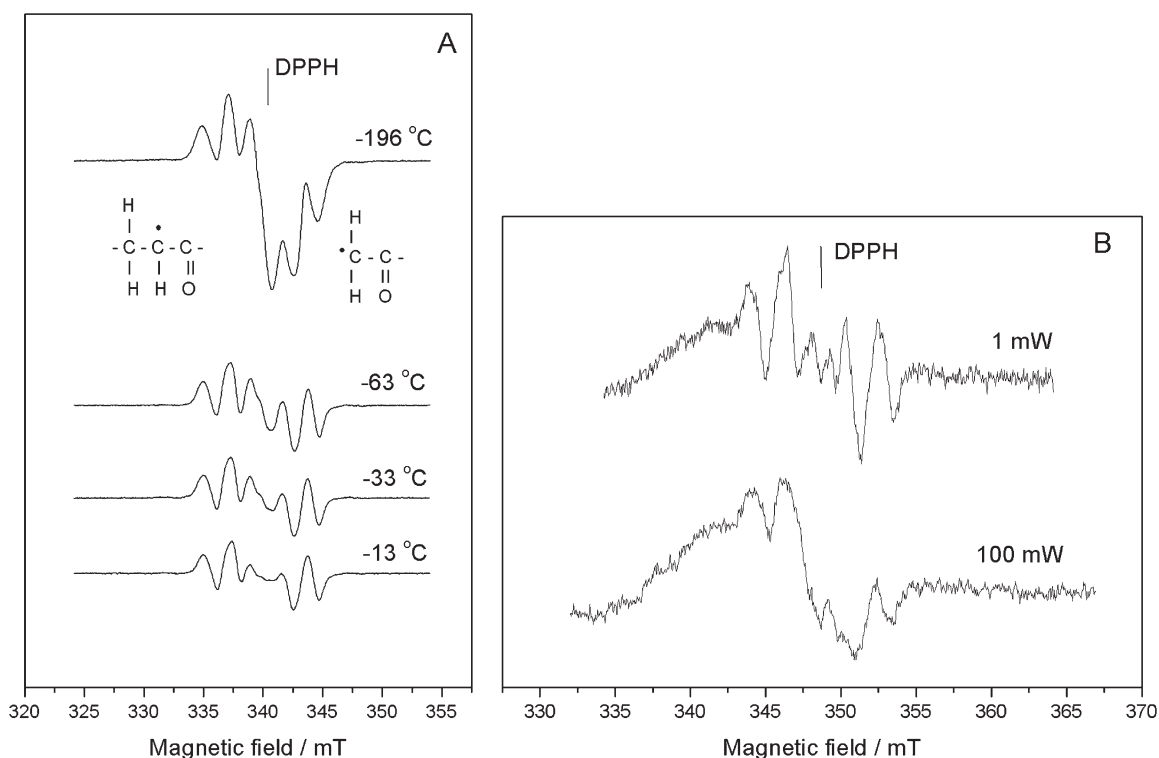


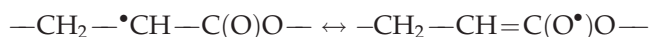
Figure 2 EPR spectra of PCL irradiated by γ -rays to a dose of 25 kGy (A) at -78°C (spectra were detected at liquid nitrogen temperature on annealing to indicated temperatures) and (B) at 23°C (spectra for two microwave powers were measured at ambient temperature).

species that subsequently, during thermal annealing, converted to secondary products. As seen from Figure 1(A) the gradual warming does not change significantly character of the signals and all spectra seem to be superposition of three components of $g = 2.0032$. Dominant doublet of hyperfine splitting (hfs) typical for alkyl radicals, 2.28 mT, might be assigned to a carbon centered radical formed on release of methyl group ($-\text{O}-\dot{\text{C}}\text{H}-\text{C}(\text{O})-$). Abstraction of hydrogen atom from third ordered carbon leads to the second paramagnetic product, $-\text{O}-\dot{\text{C}}(\text{CH}_3)-\text{C}(\text{O})-$, that shows quartet of hyperfine splitting about 2.21 mT. The same radicals were suggested earlier by Fautitano et al.¹⁸ in irradiated poly(lactide-co-glycolide). In the series of spectra recorded between -196°C and -13°C , additional lines were found - a signal of small intensity extended over *c.a.* 10 mT assigned to $\dot{\text{C}}\text{H}(\text{CH}_3)-$ intermediate of hfs = 2.41 mT appeared in the shoulders of the dominating lines and between them.^{14,18} The product possessing active center situated at the terminal group is generated via backbone cleavage and decays at lower temperatures than the radicals localized inside macromolecules as in EPR spectra of the sample irradiated at 23°C there are only signals attributed to the products of hydrogen/methyl abstraction, Figure 1(B) (spectrum recorded at 1 mW).

In addition, on an increase of microwave power to 100 mW, i.e., after partial saturation of the main spec-

tra, the new lines are disclosed. Their origin needs further investigations, however, the small absorption at $g = 2.031$ indicated in Figure 1(B) with an arrow displays presence of peroxy radical. During 24 h, all radicals decay to diamagnetic species as on the next day upon irradiation no EPR signal was found.

PCL demonstrates the EPR spectra characteristic for polyesters constructed from the linear hydrocarbon sequences between ester groups, Figure 2. The dominant component is a signal of carbon centered radical having unpaired spin localized at α position toward ester group. It was earlier found that at 23°C the anisotropic signal might be reconstructed using following parameters: $A(H_\alpha)$: 2.28; 2.01; 1.93 mT, $A(H_{\beta 1})$: 4.79; 3.72; 2.12 mT, $A(H_{\beta 2})$: 2.74; 2.78; 2.59 mT, $A(2H_\gamma)_{\text{iso}}$: 0.18 mT.¹⁹ These hfs values can be assigned to two various radicals, namely $-\text{CH}_2-\dot{\text{C}}\text{H}-\text{C}(\text{O})\text{O}-$ or $-\text{C}(\text{O})\text{O}-\dot{\text{C}}\text{H}-\text{CH}_2-$. However, it seems that the first product is more thermodynamically stable due to following resonance:



Radiation treatment carried out at -78°C was performed below glass transitions temperature of both polyesters, PLLA ($T_g \cong 60^\circ\text{C}$) and PCL ($T_g = -60^\circ\text{C}$).²⁰ Under such conditions, the chain segment motion of macromolecules is very restricted thus the radicals generated in PCL (likewise in PLLA) on

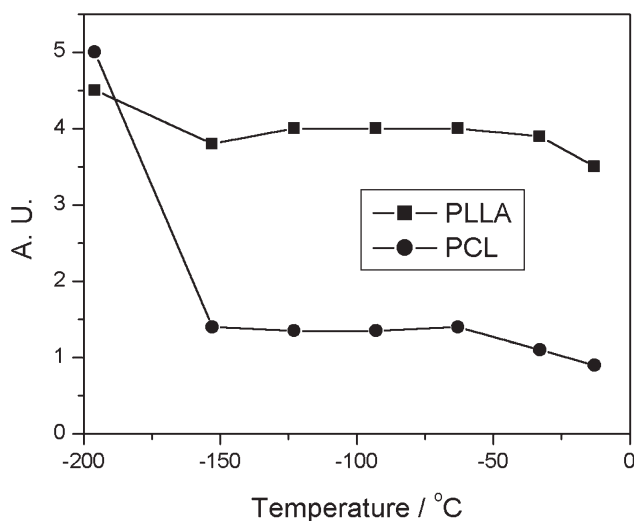


Figure 3 Radical decay in PLLA and PCL irradiated to a dose of 25 kGy at -78°C versus annealing temperature.

chain scissions are not able to convert promptly to the secondary species and show at low temperatures signal having intensive line in the center of measured magnetic field. The annealing of irradiated PCL to the temperatures close to T_g causes a noticeable decrease of the centerfield line resulting from decay of $\cdot\text{CH}_2\text{-C}(\text{O})\text{O}\cdot$ radical. Similarly, following irradiation at 23°C , i.e., above T_g , only intermediates formed upon dehydrogenation next to an ester group were found, Figure 2(B). In the recorded spectrum, characteristic low field absorption of peroxy radicals was also confirmed. High signal to noise ratio observed in the spectra measured directly on irradiation at 23°C show that the population of radicals is small, Figure 2(B). EPR measurements confirmed decomposition of the paramagnetic intermediates to nonradical products during next several hours.

As seen on Figure 3, the decay of radicals during thermal annealing is faster in PCL than in PLLA probably because of significant differences in T_g between the polymers. Consequently, thermal stability of the radicals is higher in PLLA than in PCL.

Thermal characterization

DSC experiments carried out for PCL revealed some differences in thermal characteristic of nonirradiated and irradiated materials during storage. Presented on Figure 4 results obtained during the second cycle of heating indicate that a melting point (T_m) does not change considerably on irradiation and remains almost constant with time. On the other hand, enthalpy of fusion (ΔH_m) determined by the integration of melting transition peak decreases following irradiation and the tendency slightly deepens in the course of time. It seems that not only radiation but

also aging of the irradiated samples (postradiation effect) result in partial loss of crystallinity. The effect is more apparent when PCL is irradiated at 23°C . This phenomenon probably results from radiation-induced radical processes leading to the introduction into the PCL structure new functional groups that break the regular linear sequences and initiate branching. These consequences, more intensive for the samples irradiated at 23°C , inhibit the growth of crystals during reheating. The corresponding calculated degrees of crystallinity are summarized in Table I.

The nonirradiated PLLA sample shows distinct endothermic glass transition at T_g , broad exothermic cold crystallization at T_{cc} and melting transition at T_m . Glass transition temperature of PLLA as well as melting point are at the same position before and after exposure to ionizing radiation, Figure 5. Almost constant T_g values indicate that on irradiation variations in the structure are insufficient to affect the phase transition. During the second cycle of heating, cold crystallization temperature of the samples stored for months insignificantly varies. Simultaneously, intensities of T_{cc} and T_m peaks are increasing

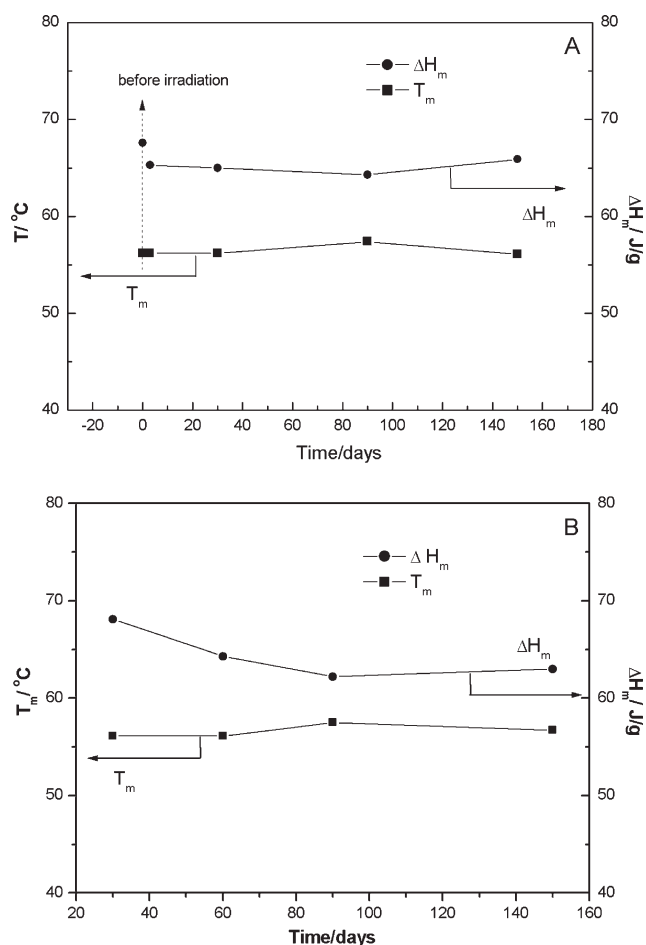


Figure 4 Changes of T_m and ΔH_m for PCL irradiated (A) at -78°C and (B) at 23°C , in the course of time.

TABLE I
Degree of Crystallinity Calculated on the Basis of Melting Transitions. Enthalpy of Fusion for Fully Crystalline Polymer: PCL - 135.2 J/g,¹⁶ PLLA - 91.0 J/g¹⁷

Time after irradiation/days	PCL			PLLA		
	Degree of crystallinity			Degree of crystallinity		
	0 kGy	25 kGy	25 kGy	0 kGy	25 kGy	25 kGy
		23°C	-78°C		23°C	-78°C
0	50%			16%		
3		50%	48%		18%	19%
30		48%	48%		34%	23%
90		46%	48%		44%	37%
150		47%	48%		41%	31%

during storage, what reveals that enthalpy of cold crystallization (ΔH_{cc}) and enthalpy of fusion (ΔH_m) enhance and the trend is even more distinct with the course of time. Thus, aging of irradiated PLLA influences morphology of the material characterized by DSC. The degree of crystallization increases after irradiation of only 2–3% but after storage the effect is significant, Table I. Degradation of selected, radiation sensitive regions initiates processes that facilitate organization of macromolecules. The short-term effect is insignificant and in accordance with some earlier studies.²⁰ Suljovrujic et al.²⁰ suggested that the radiation-induced increase in PLLA crystallinity is attributed to the scission of tie molecules and subsequently to the growth of thin-crystal structures. However, it seems that an influence of the process is possible only during exposure to ionizing radiation and that a number of tie molecule scissions in post-radiation period is insufficient to induce such a strong effect. As was calculated on the basis of enthalpy of fusion, the grow of crystalline phase enhances with time and after 150 days degree of crystallinity increases from 16% for nonirradiated sample to 41 and 31% for PLLA irradiated at 23°C and at -78°C, respectively. We did not find other reports related to the long-term radiation-induced modifications in PLLA to compare reported results with other findings. Shown DSC data refer to the samples subjected to the second run of heating, i.e., they demonstrate changes in melting that follow crystallization occurred during the first run. Thus, the results reveal the influence of the molecular modifications induced by irradiation on the ability to crystallization from the melt. The process depends on the tendency of the polymer chains to construct a regular structure. Shorter, less tangled chain molecules formed on backbone scission easier organize ordered regions. Thus, the increase in crystallinity observed as a postradiation effect might be a consequence of the progress in degradation occurred during ageing. Less probable seems to be nucleation initiated by the low-molecular products of degrada-

tion that might intensify crystallization processes. The nucleation of PLLA initiated by various agents has been reported earlier in many papers,^{21–23}

Summarizing, we confirmed following findings: irradiated PLLA demonstrates increasing ability toward crystallization with time and the effect is weaker if radiation treatment is performed at -78°C.

The changes in thermal decomposition of PCL and PLLA before and on irradiation are presented on

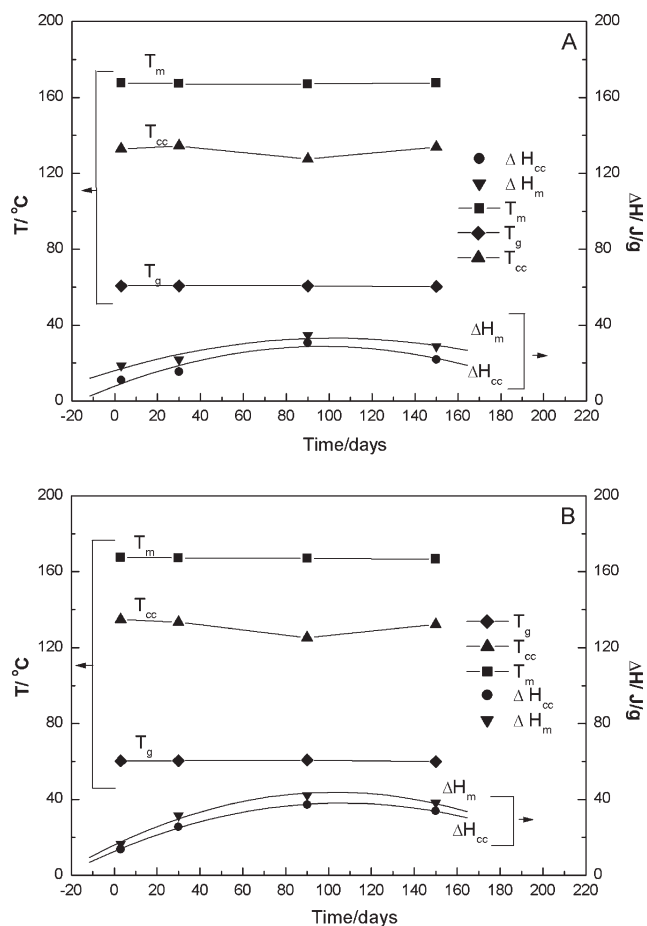


Figure 5 Changes of T_g , T_{cc} , T_m and ΔH_{cc} , ΔH_m for PLLA irradiated (A) at -78°C and (B) at 23°C, in the course of time.

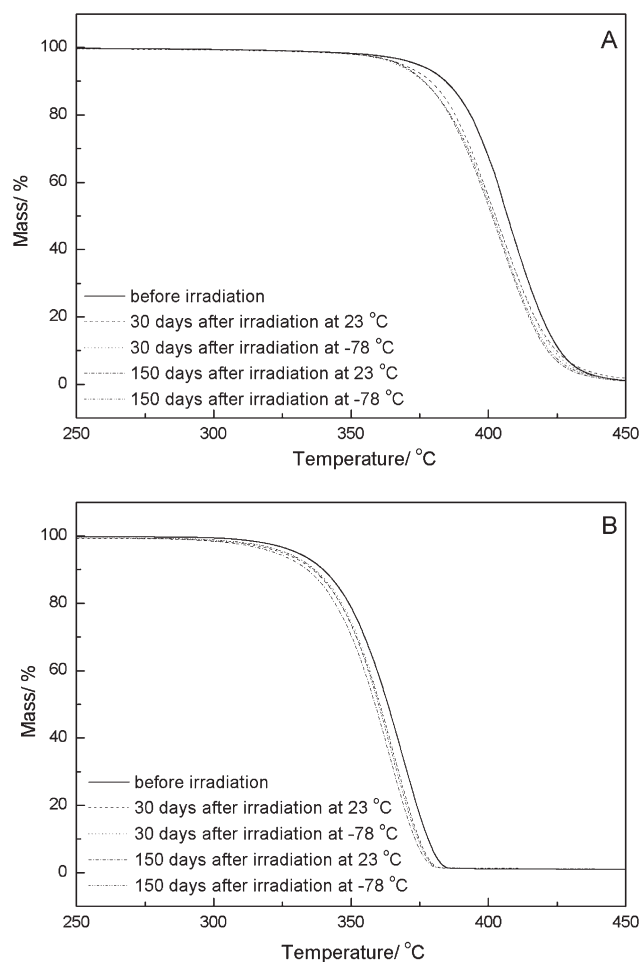


Figure 6 Thermal decomposition of (A) PCL and (B) PLLA.

Figure 6. PCL starts decaying at 350°C, whereas PLLA at about 300°C. Both relationships reveal that in the irradiated samples, due to oxidative degradation, new thermally sensitive groups are formed with time because the temperature of maximal decomposition rate for both polyesters is then shifted of about 5°C toward lower values. The thermal degradation in all cases is a single-stage process.

Rheology of polyesters

To investigate the effect of ionizing radiation on rheology of the polyesters, apparent viscosity versus time of shearing was measured, Figure 7. Three days following irradiation with a dose of 25 kGy at 23°C PCL viscosity significantly decreases, however during storage the tendency is opposite - apparent viscosity gradually increases and after 150 days reaches a level about 30 Pa·s higher than that found for the initial material. On the other hand, for PCL exposed to ionizing radiation at -78°C, the decrease in viscosity is smaller and after five months the effect

undergoes significantly restoration. It seems that the irradiated polyester is thermodynamically more stable as the detected viscosity remains constant to the end of measurement, contrary to the results obtained for nonirradiated samples.

Investigations of PLLA viscosity were performed at higher temperature than for PCL, at 230°C and 200°C, respectively, due to considerable discrepancies between melting points of the polymers. Initial viscosity of nonirradiated sample decreases more than twice during 3 min of shearing what must result from low resistance of the material on mechanical and thermal factors. The observed effect indirectly reveals difficulties expected in PLLA processing. In addition, PLLA is radiation sensitive as on irradiation with γ -rays viscosity diminishes to 20 Pa·s and 60 Pa·s, for samples irradiated at 23°C and -78°C, respectively.

In both polyesters irradiation, except degradation monitored by the rheological measurements, increases resistance on shearing and heating as the changes of apparent viscosity versus time of

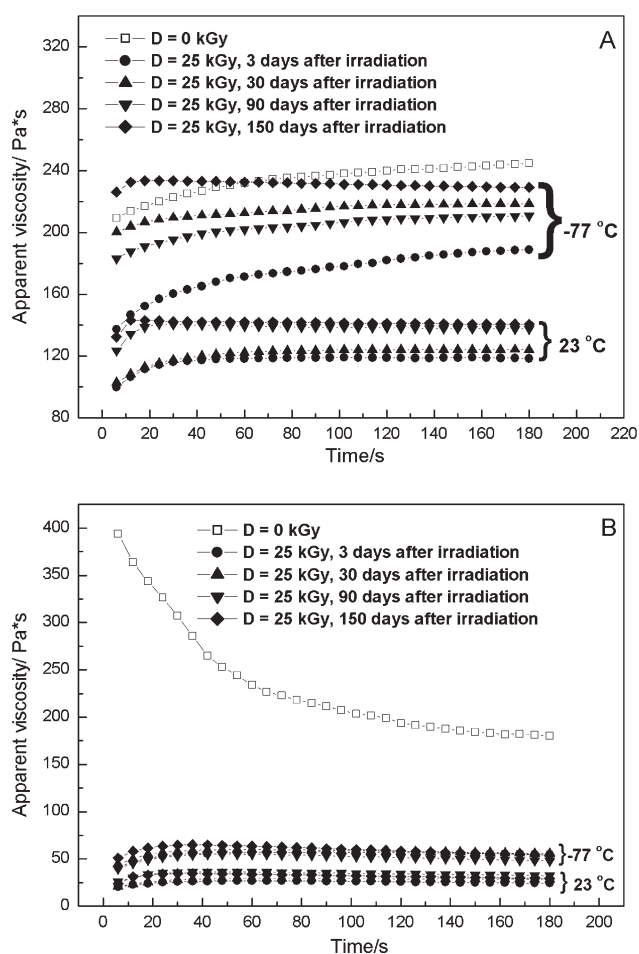


Figure 7 Apparent viscosity of PCL measured (A) at 200°C and PLLA (B) at 230°C in a function of shearing time, shear rate 40 s⁻¹, margin of error $\pm 5 \text{ Pa} \times \text{s}$.

TABLE II
Dynamic Contact Angle of PCL Versus Water at 25°C Before and After
Irradiation with a Dose of 25 kGy

Temperature of irradiation	PCL				
	0 kGy	3 days after irradiation	30 days after irradiation	90 days after irradiation	150 days after irradiation
23°C	81.2 ± 3%	83.1 ± 4%	81.0 ± 4%	83.4 ± 4%	87.0 ± 3%
-78°C		84.8 ± 4%	82.4 ± 3%	81.2 ± 3%	87.3 ± 3%

shearing are insignificant at both studied temperatures, particularly for PLLA.

Surface characteristic

Polar, oxygen containing groups formed as stable products of oxidative degradation, i.e., hydroperoxyl, hydroxyl, carbonyl, and carboxyl groups, ought to increase wettability of the samples and consequently decrease contact angle versus water. Surprisingly, on irradiation, the contact angle increases noticeable, Tables II and III, both for PCL and PLLA. It seems that ionizing radiation induces reorganization of the polymer domains, leading to the migration of hydrophobic segments toward surface. The similar phenomenon was confirmed earlier by Gorna and Gogolewski²⁴ for γ -irradiated PCL based polyurethanes. It seems that such an effect concerns predominantly hydrophobic materials as for more hydrophilic polymers exposition to ionizing radiation reduces contact angle. Mechanism of the process is still unclear.

Summary

In both studied polyesters radiation sterilization at -78°C and 23°C seems to generate analogous radicals. The EPR results indicate that the release of hydrogen, and additionally methyl group in PLLA, leads to the production of radical centers localized at α -position toward ester group. They might contribute in postradiation effects only for several hours, as afterwards, as seen from EPR measurements, the paramagnetic species decay completely. Further transformations of the esters are initiated by diamagnetic products of degradation/oxidation.

On exposition to ionizing radiation both at 23°C and -78°C population of the paramagnetic species is higher in PLLA than in PCL. Part of terminal radicals formed as a result of chain scission generated at -78°C, i.e., below T_g , are trapped close to each other at a rigid matrix, therefore the restoration of the ruptured chain via radical recombination is possible. The effect is smaller for the samples irradiated at ambient temperature when due to local thermal motions the chain ends might escape from the initial position. In consequence, degradation initiated by irradiation is more efficient at 23°C than at lower temperature.

Morphology of irradiated PCL and PLLA determined by DSC changes in the opposite directions. As it was observed during the second cycle of heating, crystallinity of PLLA increases, probably due to backbone scissions leading to the reduction of limitations in the relocation of chain ends. The PLLA structure is stiff and constructed in turns from ester and methylene units. In addition, pendant methyl groups regularly situated at the same position support the ordering of mers, particularly when long chain of macromolecules are getting shorter due to gradual degradation during aging. On the other hand, in much shorter PCL macromolecules, the hydrocarbon linkage containing five methylene groups makes the chains more flexible. Thus, during cooling terminal fragments might remain in the amorphous regions diminishing degree of crystallinity.

Advantages of radiation sterilization at -78°C were confirmed by apparent viscosity measurements. Both studied polyesters, PCL, and PLLA, degrade on γ -radiation with a dose of 25 kGy. An extend of the process is limited if the sample is

TABLE III
Dynamic Contact Angle of PLLA Versus Water at 25°C Before and After Irradiation
with a Dose of 25 kGy

Temperature of irradiation	PLLA				
	0 kGy	3 days after irradiation	30 days after irradiation	90 days after irradiation	150 days after irradiation
23°C	89.1 ± 3%	85.3 ± 3%	89.8 ± 4%	88.4 ± 3%	94.4 ± 3%
-78°C		88.0 ± 4%	85.6 ± 3%	89.0 ± 3%	95.6 ± 2%

exposed to ionizing radiation at -78°C , since in such a case the reduction of apparent viscosity is smaller than for samples irradiated at 23°C . Surprisingly, with the course of time, viscosity of melted PCL increases. The process can not be initiated by the radicals detected by EPR spectroscopy as on the second day following irradiation there are no paramagnetic species, both in PCL and in PLLA. Thus, during heating, in the stored samples other transformations are supposed to be considered, e.g., conversion of hydroperoxides into oxygen containing bridges formed between two chains. Hydroperoxide is stable, oxygen containing group that decomposes at relatively low temperatures forming oxygen centered radicals that might easily recombine particularly at elevated temperatures facilitating cross-linking and subsequently increasing viscosity. The production of oxygen containing groups was confirmed by EPR technique as well as by the TGA experiments that demonstrate that the thermal decay of irradiated polyesters starts at lower temperatures than nonirradiated ones. The population of hydroperoxide increases with time as a consequence of progressive oxidative degradation. Therefore, during storage, capability of PCL toward production of oxygen containing linkages between chains increases as was confirmed on a basis of apparent viscosity studies. The cross-linking is probably to some extent responsible for small decrease in PCL crystallinity observed during the second run of DSC experiments. Such a process is limited in the irradiated PLLA due to steric obstacles (pendant methyl groups) thus, in this polyester, formation of oxygen containing bridges is negligible and could not inhibit the growth of crystalline phase.

From practical point of view in these series of experiments it was found that (i) γ -sterilization initiates predominantly degradation both in PLLA and PCL but the former polyester is more radiation sensitive, (ii) exposure to γ -rays at dry ice temperature limits this process, (iii) during postradiation ageing morphology and rheology of the studied polyesters are strongly affected thus their features ought to be controlled with time, and (IV) insignificant but

undesired loss in hydrophilic properties of PCL and PLLA surfaces was confirmed.

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