Effects of UV radiation on some properties of dyed polylactide film

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Abstract: The effects of the UV radiation on the surface geometrical structure, phase transition temperatures, and the temperature of the onset of thermal decomposition of a polylactide film containing 2 wt % of dye are presented. The surface geometrical structure was examined using a scanning electron microscope (SEM) and atomic force microscope (AFM). The temperatures of both the phase transitions and the changes in the melting enthalpy of the crystalline phase were determined using a differential scanning calorimeter (DSC). The temperature of the onset of thermal decomposition of the film was determined with a thermogravimetry (TG) instrument. It was found that the UV radiation generated in an aging test chamber mostly causes changes in the surface geometrical structure of the examined film and reduces the onset temperature of the film thermal decomposition.

Keywords: biodegradable polymers, polylactide, UV aging, scanning electron microscopy, atomic force microscopy, differential scanning calorimetry, thermogravimetry.

Wpływ promieniowania UV na wybrane właściwości barwionej folii polilaktydowej

Streszczenie: Przedstawiono wpływ promieniowania UV na strukturę geometryczną powierzchni, temperaturę przejść fazowych i temperaturę początku rozkładu cieplnego folii polilaktydowej zawierającej 2 % mas. barwnika. Badania struktury geometrycznej powierzchni wykonano metodami skaningowej mikroskopii elektronowej (SEM) oraz mikroskopii sił atomowych (AFM). Za pomocą różnicowego kalorymetru skaningowego (DSC) wyznaczano temperaturę przejść fazowych i zmian entalpii topnienia fazy krystalicznej. Temperaturę początku rozkładu cieplnego folii badano przy użyciu termograwimetru (TG). Stwierdzono, że promieniowanie UV, generowane w komorze starzeniowej, zmienia głównie strukturę geometryczną powierzchni folii oraz obniża temperaturę początku jej rozkładu.

Słowa kluczowe: polimery biodegradowalne, polilaktyd, starzenie UV, skaningowa mikroskopia elektronowa, mikroskopia sił atomowych, różnicowa kalorymetria skaningowa, termograwimetria.

Polymeric materials that are being used to manufacture packaging play an important role in the global economy. Among them, polyolefins dominate mainly due to easy processing, low cost, application versatility, and lack of harmful effects on living organisms. However, a growing mass of waste being a load to the natural environment is an undesirable result of a dynamic development of the packaging market involving these polymers [1, 2].

Polylactide (PLA), being polyester, belongs to a group of biodegradable polymers. It is now more and more often applied in industry as a material used to manufacture food packaging as well as fishing nets, clothes, and underwear [3–5]. PLA is being produced from natural resources, *e.g.*, corn, soybean, or grain. It undergoes biodegradation caused by microorganisms (yeasts, bacteria, fungi, or mildew) as quickly as within a dozen or so days at suitable humidity and temperature of the environment [6, 7]. Therefore, packaging made of biodegradable materials does not create persistent environmental pollution [8].

Resistance to UV irradiation, or aging resistance, is an important feature of polymeric materials, relating to their functional quality. This feature is examined in aging test chambers, enabling precise setup of conditions of accelerated aging. The aging of polymeric materials includes physical and chemical changes that affect properties of these materials important for processing, storage, and utilization. This process leads most often to irreversible changes in the physical and chemical structures of these polymers, resulting in worsening of their processing properties. Thus, the aging unfavorably affects functional qualities of polymers, especially their durability, reliability, and esthetic values [9–12].

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When exposed to the natural environment, polymeric materials undergo mostly photodegradation, biodegradation, and hydrolytic degradation [13–16]. Photodegradation studies are of practical importance because the articles made of polymeric materials are frequently exposed to the sunlight, causing unfavorable changes in their performance.

The purpose of the present work was to determine effects of accelerated aging of a dyed PLA film upon UV radiation on the surface geometrical structure, phase transition temperatures, and onset temperature of thermal decomposition of this film.

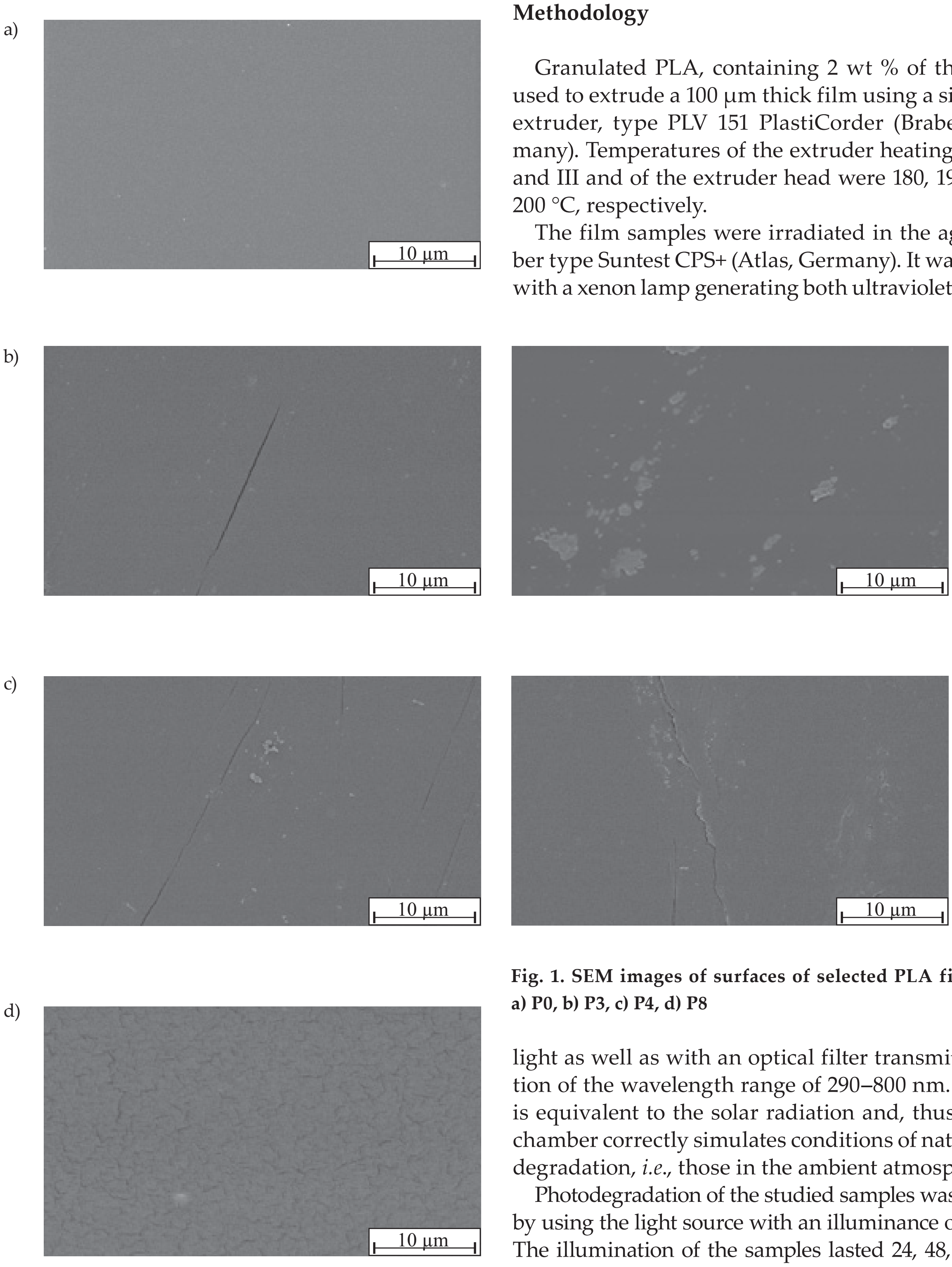

Fig. 1. SEM images of surfaces of selected PLA film samples: a) P0, b) P3, c) P4, d) P8

EXPERIMENTAL PART

Materials

Polylactide (PLA), type 2002D (NatureWorks®, USA), composed of monomeric units D (3.5 %) and L (96.5 %), with the melt flow rate of 4.2 g/10 min (2.16 kg, 190 °C) and density of 1.24 g/cm^3.

Green dye, type 79599 GN BIO1, masterbatch on PLA matrix (PolyOne, USA), specified elsewhere [17].

Methodology

Granulated PLA, containing 2 wt % of the dye, was used to extrude a 100 µm thick film using a single-screw extruder, type PLV 151 PlastiCorder (Brabender, Germany). Temperatures of the extruder heating zones I, II, and III and of the extruder head were 180, 190, 200, and 200 °C, respectively.

The film samples were irradiated in the aging chamber type Suntest CPS+ (Atlas, Germany). It was equipped with a xenon lamp generating both ultraviolet and visible light as well as with an optical filter transmitting radiation of the wavelength range of 290–800 nm. This range is equivalent to the solar radiation and, thus, the aging chamber correctly simulates conditions of natural photodegradation, *i.e.*, those in the ambient atmosphere.

Photodegradation of the studied samples was performed by using the light source with an illuminance of 756 W/m^2. The illumination of the samples lasted 24, 48, 72, 96, and

192 h at 65 °C, under forced air circulation. The sample illuminated for 24 h absorbed the radiation dose of 66 095 kJ/m^2, while that irradiated for 192 h – the dose of 528 760 kJ/m^2. The samples illuminated for 0 (non-irradiated), 24, 48, 72, 96, and 192 h were denoted as P0, P1, P2, P3, P4, and P8, respectively.

Methods of testing

Changes in the surface geometrical structure of the samples were examined by using scanning electron microscope (SEM), type Hitachi SU8010 (Hitachi High-Technologies Co., Japan). SEM that enabled cold cathode field emission and was equipped with 4 detectors: two SE, BSE, and EDX.

To determine the mentioned changes atomic force microscope (AFM), type Nanoscope IIIa (Digital Instruments, USA), in a tapping mode, was applied as well according to the standard PN-EN ISO 4287:1999.

The phase transition temperatures and changes in the melting enthalpy of the crystalline phase were determined using differential scanning calorimeter (DSC), type Q200 (TA Instruments, USA), according to appropriate standards: PN-EN ISO 11357-1:1997, ISO 11357-2:1999 and ISO 11357-3:1999.

The thermogravimetry curves [TG device, type Q500 (TA Instruments, USA)] were recorded according to a suitable standard PN-EN ISO 11358:2004, at a heating rate of 10 K/min and over the temperature range of 0–600 °C.

RESULTS AND DISCUSSION

SEM investigation

SEM images of surfaces of the non-irradiated sample (P0) and samples (P3, P4, and P8) irradiated in the aging chamber are shown in Fig. 1.

As can be seen, scratches and cracks appeared on the surfaces of the irradiated film samples. These features are already seen on the image of the sample P3 irradiated for 72 h. The number and sizes of the scratches, cracks, and pinholes increase as the irradiation time rises, which is especially evident in the case of sample P8. Darkening and tarnishing of sample surfaces increase with a growing UV dose as well, being a result of formation of a dense net of cracks, visible particularly distinctly on the sample P8 image (Fig. 1d). These observations agree with the results of our earlier studies [11] and with images of the surface of a polymer-wood composite aged in a Xenotest device [18].

AFM investigation

Surface images, surface roughness profiles, and values of root-mean squared (RMS) roughness (according to PN-EN ISO 4287:1999) of individual PLA film samples as derived by AFM are shown in Figs. 2 and 3.

The figures demonstrate that surfaces of the aged samples exhibit numerous scratches and cracks. It was also found that the RMS value corresponding to the roughness of the studied film samples varies from 1.6 nm for sample P0 to 3.5 nm for sample P8, *i.e.*, it increases as the radiation dose rises.

DSC investigation

The effects of the aging of PLA samples on the temperatures of phase transitions and changes in melting enthalpy were determined from the DSC curves relating to both the first and the second heating cycles (Figs. 4 and 5).

The DSC curves relating to the first heating cycle reveal changes associated with the glass transition, cold

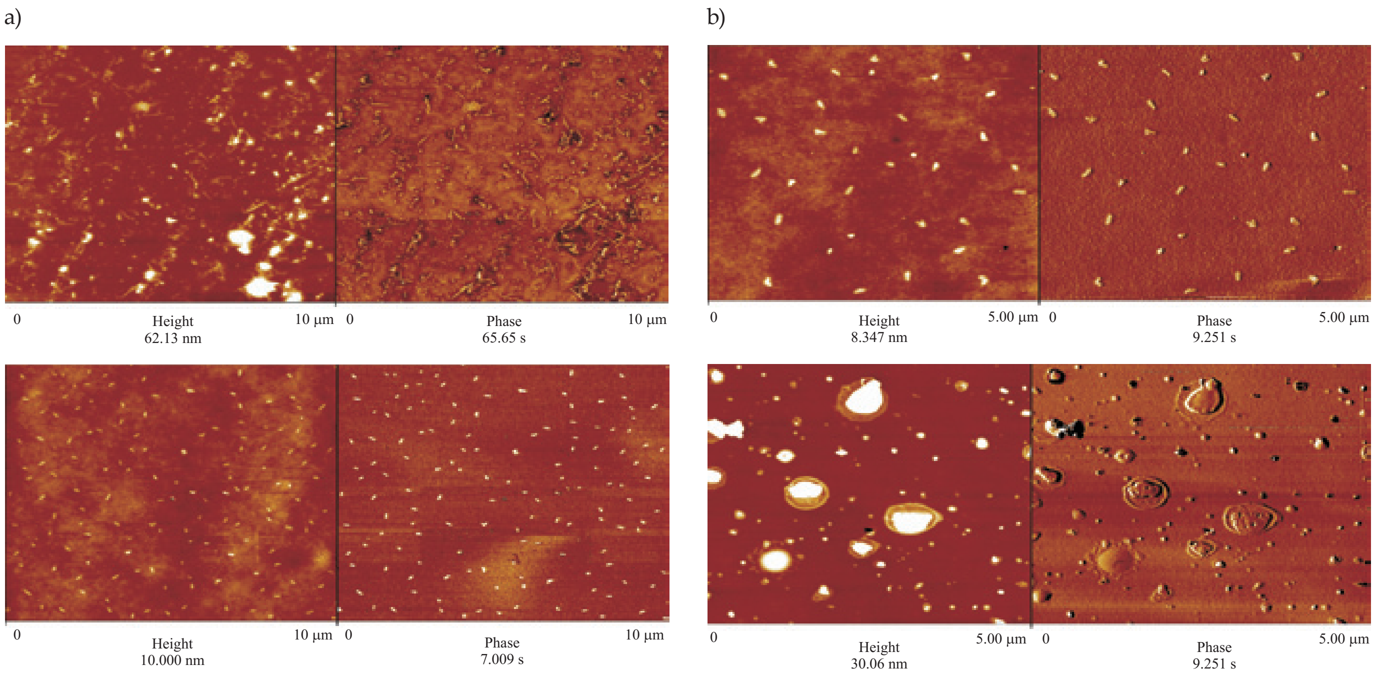

Fig. 2. AFM images of surfaces of selected PLA film samples: a) P4, b) P8

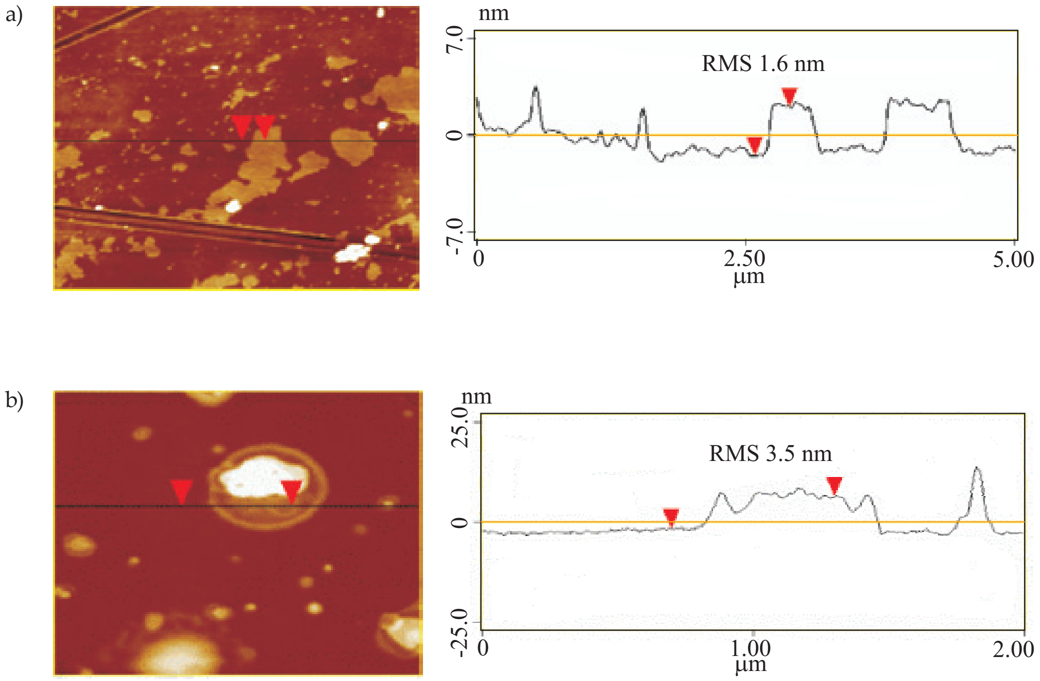

Fig. 3. AFM images of surfaces of selected PLA film samples, surface roughness profiles, and values of root-mean squared roughness: a) P0, b) P8

crystallization, and melting of the crystalline phase. The shapes of the DSC curves vary with the rising aging time. As derived from the curves, the glass transition temperature (T_g) increases from 61.7 °C (sample P0) to 66.0 °C (sample P8). Also, enthalpy of the endothermic peak attributed to stress relaxation increases from 4.7 J/g (sample P0) to 8.4 J/g (sample P8). Furthermore, the aging process causes changes in the course of cold crystallization, which manifests itself in flattening of the peak assigned to that crystallization. This is accompanied by an increase in the temperature (T_{cc}) corresponding to the maximum of the cold crystallization peak from 129.3 °C (sample P0) to 132.2 °C (sample P8) and increase in the enthalpy (ΔH_{cc}) of that process from 2.9 J/g (sample P0) to 3.9 J/g (sample P8).

The DSC curves concerning the second heating cycle show changes connected with the glass transition and melting of the crystalline phase. The peaks ascribed to the stress relaxation and cold crystallization do not appear. Disappearance of the stress relaxation peak is typical of the situation when a thermal history of a polymer has been cleared as a result of the second heating.

Analysis of the DSC curves relating to the second heating shows that the aging process causes no essen-

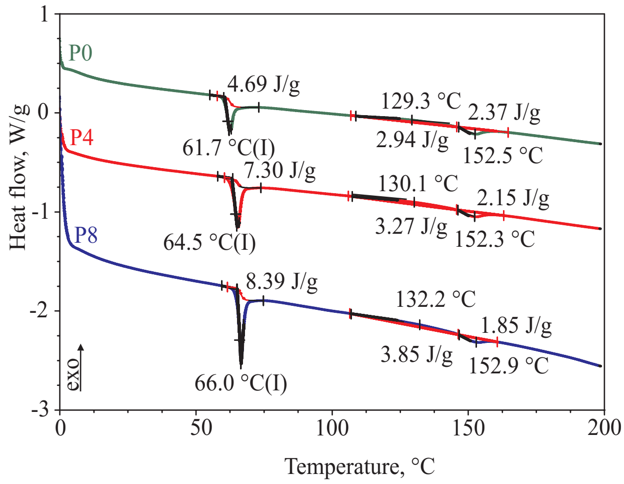

Fig. 4. DSC curves of the first heating of selected PLA film samples: P0, P4, and P8

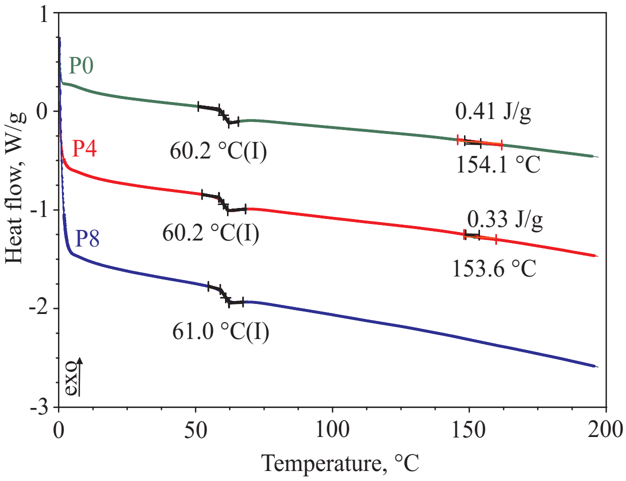

Fig. 5. DSC curves of the second heating of selected PLA film samples: P0, P4, and P8

tial changes in the glass transition temperature of the PLA film samples. The T_g value of these samples is *ca.* 60.2 °C. Prolonged aging results in slight increasing in T_g (to 61.1 °C for sample P8).

The melting enthalpy (ΔH_m) of sample P0 is 0.4 J/g. The aging process causes a decrease in that value to, *e.g.*, 0.3 J/g for sample P4. A relatively long aging time results in a total decay of the crystalline phase.

TG investigation

The thermogravimetry curves of samples P0, P4, and P8 are presented in Fig. 6.

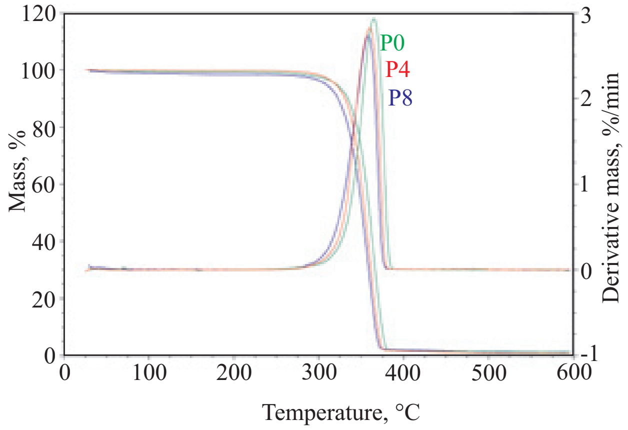

Fig. 6. TG curves of selected PLA film samples: P0, P4, and P8

The curves shown in Fig. 6 indicate that the temperature (T_d) of the onset of thermal decomposition of the PLA film samples decreases from 343.7 °C (sample P0) to 334.7 °C (sample P8) as the aging time increases.

CONCLUSIONS

The accelerated aging for up to 192 h of a dyed PLA film upon UV radiation mostly consists in a change in the surface geometrical structure. Numerous cracks and scratches and a dense net of fractures appear on the film surface. As a result, the root-mean squared roughness of the film surface increases by a factor of more than 2.

The accelerated aging of a dyed PLA film upon UV radiation does not cause significant change in the glass transition temperature determined from the second heating curve. The temperature of the onset of thermal decomposition of the film becomes distinctly reduced (by *ca.* 9 °C). A relatively long aging time results in a total decay of the crystalline phase.

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