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ORIGINAL PAPER

Using depolarized light intensity to study the crystallization and degradation behavior of poly(L-lactic acid) and its blends with poly (ethylene oxide)

Xiaocan Zhang[1] · **Kathy L. Singfield**[2] · **Haimu Ye**[1]

Abstract The crystallization and degradation behaviors of poly(L-lactic acid) (PLLA) and its blends with poly(ethylene oxide) (PEO) were investigated by depolarized light intensity (DLI). It was found that DLI is sensitive to study the degree of order in polymer thin film samples. The growth rate of the PLLA spherulites was increased by blending up to 80 % PEO, as it increased the chain mobility in the blend melts. At larger PEO compositions (i.e., 90 % PEO), the dilution effect dominates and the PLLA growth rate was retarded. Three distinct blend groups with respect to the blend composition were proposed: (1) 10–20 wt% PEO in which the PEO is not able to form any ordered structure in the binary blend; (2) 30–50 wt% PEO in which the PEO is able to form some order but not enough to develop spherulitic crystals; (3) 60–90 wt% PEO in which the PEO forms a network of spherulites throughout the pre-crystallized PLLA.

Keywords Poly(L-lactic acid) · Poly(ethylene oxide) · Blend · Depolarized light intensity · Crystallization · Enzymatic degradation

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Introduction

As polymers exhibit different morphologies in terms of degrees of order, changes in the physical property of birefringence can be applied to examine the thermal behavior of polymer thin film samples, based on changes in morphology.

The intensity of the depolarized light increases with increasing order in the sample as the chain-folded lamellae are what give rise to the birefringence, before finally being extinguished by the melted sample. Therefore, the measured intensity of the total transmitted depolarized light can be used to monitor the changes in the relative crystallinity of spherulites during heating, melting, annealing, and crystallization [1–8]. When measured at regular intervals during a phase change, this property provides a unique perspective of melt crystallization of polymer spherulites as well as their thermal behavior during melting.

The use of depolarized light intensity (DLI) offers simultaneous morphological observation [5]. It is also reported to have a short response time, and potentially useful to study crystallization processes that are too fast to be followed by measurements such as density, X-ray diffraction and calorimetry [9]. The excellent sensitivity of depolarized light on interphase may be used to correlate optical data [10] and semiquantitatively study complex systems.

In this study, DLI measurements were used to study the crystallization and degradation behaviors of PLLA and its blends with PEO, which were extensively examined by other techniques in various research groups [11–15]. At the crystallization temperatures chosen in this paper, PLLA crystallized while PEO remained in melt. The amorphous state of PEO, having been expelled from the PLLA crystals, alters its interaction with light during the cool, and could be recorded by DLI.

The DLI heating profile would illustrate the effect of crystallization (and degradation) on the polymer's natural tendency to undergo a cold crystallization during the heating scan. An enzyme has been used to introduce degradation of PLA, and it was believed that the enzyme would attack the relatively disordered fold surfaces of the lamellae in the spherulites and effectively render that relatively amorphous part of the inter-lamellar regions, which is, therefore, unable to be part of the reordering process. An increase in internal order of the spherulite as a result of any reorganization or annealing of the chains during heating would be reflected in an increase in birefringence which in turn would be manifested in an increase in the intensity of the depolarized light transmitted by the sample.

The objective of this work is to investigate crystallization and degradation mainly using DLI, so as to study how PEO resides in its blends with PLLA in thin film samples.

Materials and methods

Materials

Poly(L-lactic acid) (PLLA, $M_w = 50,000$ g/mol) and purified tris(hydroxymethyl) aminomethane (TRISMA) were purchased from Polyscience Inc., and Fisher

Scientific Company, respectively. Poly(ethylene oxide) (PEO, $M_v = 100,000$ g/mol) and Proteinase K (EC 3.4.21.64, 36 units/mg protein) were bought from Sigma-Aldrich. The melting points of PLLA and PEO are measured to be 178 and 65 °C, respectively.

Sample preparation

The blends in this study were prepared by mixing appropriate quantities of each polymer in dichloromethane and shock precipitated using ethyl ether. After centrifuging, all samples were dried and stored under vacuum. In this way, the following compositions were prepared (in the ratio of weight % PEO/weight % PLLA): 0/100 (pure PLLA), 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10, and 100/0 (pure PEO).

Polymer thin films were prepared using melt-pressing technique. A small amount of the sample was placed on a microscope glass coverslip and preheated to 200 °C till it became translucent, a second coverslip was then quickly put on top with downward pressure to form a sandwiched polymer thin film. The sandwiched sample was rapidly removed from the hot surface and placed on the bench to cool and it remained at room temperature until use. All samples were fresh made and the resultant thickness was in the range of 8–15 μm. For open-face samples, the two cover slips were split apart immediately upon removal from the hotplate, so that the thin film was only on one coverslip.

Proteinase K (0.042 %wt/vol) enzyme was added to the 50 mM Tris–HCl (Tris(hydroxymethyl) aminomethane–HCl) buffered solution as the degradation medium.

Characterizations

A Nikon Coolpix 4500 digital camera was mounted on the trinocular tube of a Nikon Eclipse E400 POL polarized light optical microscope (POM), and equipped with a Linkam TMS 94 temperature controller for this study. All samples were held at 200 °C for 1 min to erase the thermal history, and were then cooled at 70 °C/min to the crystallization temperature for a controlled period of time.

The crystallization, degradation and melting of polymer thin films were qualitatively examined by measuring the total depolarized light transmitted by the sample. The DLI transmitted by the sample was recorded using a Mettler photomonitor in tandem with a Mettler FP80 central processor. One ocular of the microscope was replaced with this photomonitor. The photomonitor was calibrated for zero DLI by totally dark, and for half of the maximum intensity using a completely crystallized sample.

A buffered aqueous solution of Proteinase K enzyme was used as a degradation medium for thin film samples with unrestrained (open-face) crystallization. The crystallized polymer sample was placed in the crucible. Using an Eppendorf pipette, a volume of 480 μL of the 0.042 %wt/vol Proteinase K solution was added to this crystallized polymer sample by effectively filling the crucible. An 18-mm-diameter microscope glass coverslip was set on top to keep the solution from evaporation.

The samples were maintained at 37 ± 0.1 °C using the Linkam hotstage for a controlled period of time. After exposure to the degradation medium for the desired amount of time, the liquid on top of the sample was syringed off and the remaining wetness was removed by gentle capillary action using a Kimwipe tissue. The coverslip-supported film was then removed from the crucible holder for further use.

Results and discussion

Crystallization and degradation behavior of crystallized PLLA

The DLI measurement of polymer thin films was undertaken to investigate the degree of order within the sample. To carry out a systematic investigation, factors such as DLI sensitivity, its applicability in both degraded and non-degraded samples, as well as its correlation with routine technique were considered.

Figure 1 shows the DLI heating profiles of PLLA thin film samples with a thermal history of isothermal crystallization at 147 °C for 80 min, followed by cooling down to room temperature. The heating rate was varied from 2 °C/min to 20 °C/min. It can be seen that the light intensity has an obvious upturn in the temperature range of 90–120 °C for all the profiles. The upturn in intensity signifies an onset to an ordering process within the sample during heating, corresponding to the cold crystallization process of PLLA. The figure also shows that the slower the heating rate, the earlier this upturn begins. The effect of heating rate on the profile can be justified by the fact that the polymer chains have more time to reorganize themselves at slower heating rate. The disappearance of polymer crystals corresponds to the abrupt drop in light intensity at around 180 °C, and signifies the complete melting of PLLA.
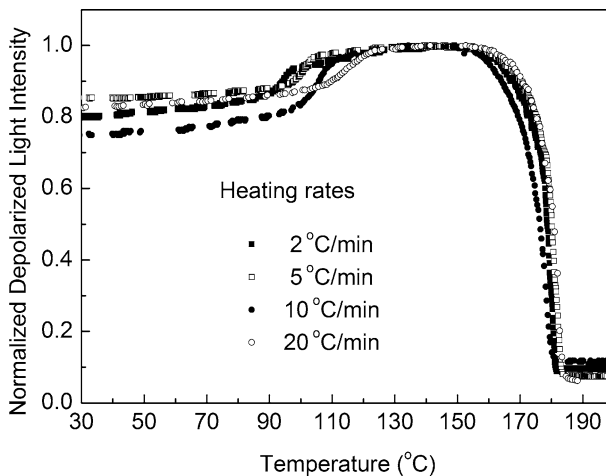

Fig. 1 DLI heating profiles of PLLA at different rates. All samples crystallized as open-face thin films at 147 °C for 80 min. The *error bar* is within the size of the data points

There is another phenomenon worth noticing. The PLLA samples were crystallized at 147 °C while reorganized themselves at lower temperatures (i.e., 90–120 °C). The portion formed at high temperatures should not reorder at lower temperatures; rather, it is possible that some crystals had less perfection or even non-crystallized amorphous region existed. It is well known that spherulites crystallized at lower temperature posses a lower degree of crystallinity and thinner lamellar thickness, and a greater tendency to reorganize during subsequent heating. It is possible that the 80-min period was too short for a complete crystallization, and apparent amorphous regions are still present. Upon cooling process, new crystals with less perfection formed. These newly formed crystals or non-crystallized amorphous region might be responsible for the upturn in Fig. 1.

The results in Fig. 1 confirmed the sensitivity of the DLI to internal changes in order. Since profiles obtained at all heating rates were sensitive to these changes, a heating rate of 10 °C/min rate was chosen for following measurements.

Different degradation periods were investigated to examine the applicability of DLI to study degraded samples. A set of experiments was performed in which only the degradation time period varied from 0 to 8 h. The subsequent DLI heating profiles from selected degradation times were compared and are illustrated in Fig. 2. It can be seen that all of the DLI profiles demonstrate increasing intensity with heating until they finally melt with abrupt drop in intensity. All of the samples exposed to enzyme solution show a slow and steady increase. The sample that was not exposed to enzyme solution has an added feature as those profiles shown in Fig. 1. This sample exhibits an onset to the upward step at around 100 °C. The lack of the upturn in the profiles of samples exposed to enzyme solution is believed to be an effect of enzymatic degradation. The absence of the upturn step indicates no onset to reorganization, which signifies that no obvious amount of amorphous material or imperfect crystals is able or available to reorganize.
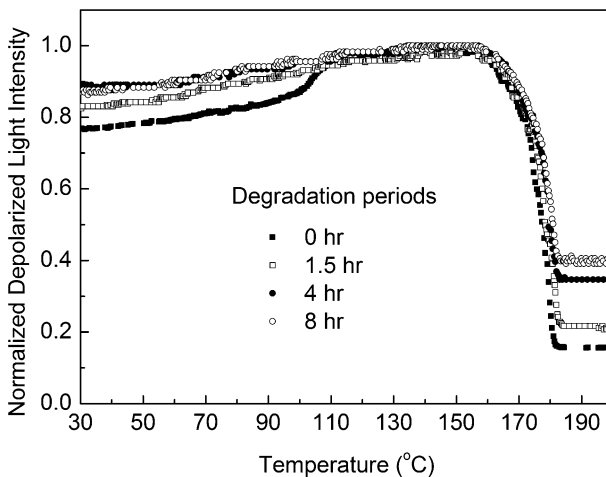

Fig. 2 DLI heating profiles (10 °C/min) of PLLA following enzymatic degradation for different periods according to legend. All samples crystallized as open-face thin films at 147 °C for 80 min prior to degradation. The *error bar* is within the size of the data points

For the DLI profiles of enzyme-affected films, it can be postulated that a certain amount of amorphous areas had been cleaved by enzyme during the degradation period. The cleaved amorphous PLLA chains were decomposed into lower molecular ones which could either stay in the places where they were or be removed with the enzyme solution after degradation. In the first case, the chains are not able to reorganize because the enzymatic chain scission has made them too short to crystallize.

It is also noticeable that DLI did not drop to zero after all crystals eventually melted around 190 °C. DLI signals remained at higher values with longer degradation periods. Enzyme randomly scissored the polymer chains, and longer degradation periods would have wider diversity of chain lengths. Therefore, it is reasonable to propose that the changes in residual DLI might indicate the appearance of boundaries (i.e., interphase), which is caused by phase separation between high and low molecular weight PLLA fractions. These boundaries would be easier to be detected by DLI but not by optical microscopy.

To further probe the origin of the apparent upturn in the DLI profiles, another set of experiments was performed in which the thermal history was changed: a crystallization temperature of 130 °C was used. The crystallization time remained for 80 min, because it was found using DLI method during crystallization that the sample reached its maximum DLI value within this time period (less than 60 min). In this set of experiments, the variable of degradation time was changed from 0.5 to 12 h. An extreme run was also applied with a higher concentrated enzyme solution (0.15 %wt/vol) and for a much longer degradation time (17 h).

First, DLI signals after melting still agreed with what is shown in Fig. 2, that is, total disorder transmitted depolarized light. In addition, the remained light intensity increased with longer degradation periods, or more concentrated enzymatic solution. The phenomena also indicated the formation of interphase caused by the scission of polymer chains.

All DLI profiles in Fig. 3 lack the sudden upturn steps around 100 °C, and can be discussed considering the images presented in Fig. 4. The images in Fig. 4a, b are representative of what the samples looked like at room temperature after 80 min of isothermal crystallization at 147 and 130 °C, respectively. While the sample in Fig. 4b shows that the spherulites had grown to the point of impingement, there remained significant amount of non-crystallized polymer melt in Fig. 4a. It is evident that this non-crystallized material remained amorphous during the cooling to room temperature and which would be most vulnerable to reorganization during subsequent heating. The characteristic upturn feature in preceding DLI profiles is attributed to the cold crystallization of PLLA. The Fig. 4b sample had totally crystallized and, therefore, showed no upturn step in Fig. 3. The slow and steady increase of DLI profiles in Figs. 2, 3 was systematic and might be related to thermal expansion.

Upon closer examination (shown in inset of Fig. 3), an upturn was evident for the non-degraded sample. Since there was no obvious free amorphous region under this condition (Fig. 4b), this upward step is proposed to be caused by the cold crystallization of confined amorphous phase to form crystallites, which was difficult to characterize under POM. In this regard, DLI is superior to POM in the
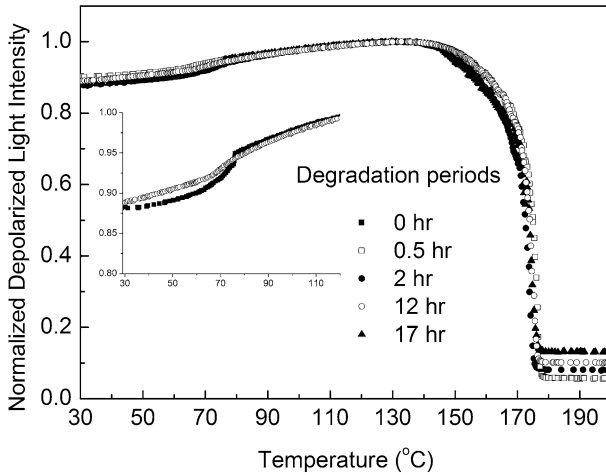
Fig. 3 DLI heating profiles (10 °C/min) of PLLA following enzymatic degradation for different periods according to legend. The *inset* figure depicted the enlarged area in the temperature range of 90–120 °C, comparing the non-degraded sample with sample degraded for 12 h. All samples crystallized as open-face thin film samples at 130 °C for 80 min. The *error bar* is within the size of the data points
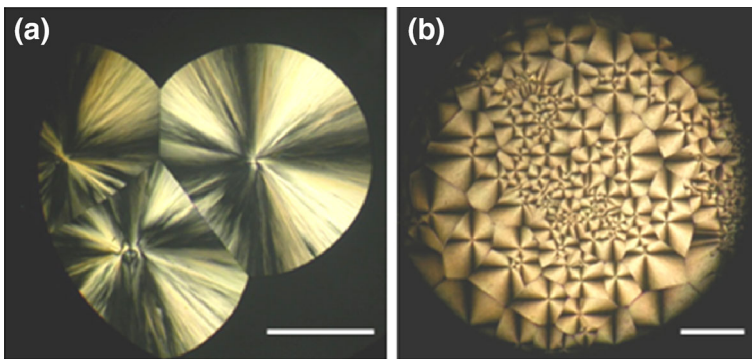

Fig. 4 Polarized light optical micrographs of PLLA spherulites crystallized at (**a**) 147 °C and (**b**) 130 °C both for 80 min, followed by cooling to room temperature on bench. *Scale bar* 300 μm in **a** and 600 μm in **b**

examination of the appearance of crystallites. This feature might help to study the crystallization and degradation behavior of PLLA upon blending with PEO using DLI.

It is also noticeable that this upturn (in inset) occurred at a lower temperature than that in Fig. 2. Both samples were not immersed in enzymatic solution and the only difference was the crystallization temperature (T_c). At lower T_c (i.e., 130 °C), the already formed crystals (i.e., impinged spherulites) facilitated the self-nucleation to develop crystallites, which consequently showed an earlier upward step.

It is concluded that DLI is useful to study the degree of order in crystallized as well as degraded samples. The polymer solid structure increases the order, which is reflected by the rise in DLI, before it finally melts. The detected and analyzed features were authentic and more sensitive than acquired by POM.

Crystallization and degradation behavior of PEO/PLLA blends

In an effort to open up the internal structure of PLLA, and expose the relatively disordered fold surfaces of the lamellae building blocks to the enzyme, and perhaps improve its biodegradability, a second polymer was added to PLLA. A blend of two polymers, PLLA and PEO, was made. PEO is unique in its water solubility and thus might enhance the enzyme penetration ability to allow for those internal areas of the PLLA spherulite to be exposed to the degradation medium. While PEO is crystallizable, it remains amorphous at the crystallization temperature (T_c) of PLLA. Thus, at the T_c of PLLA the blend behaves as a crystalline/amorphous polymer blend. With subsequent cooling to room temperature, however, the PEO passes through its own T_c region while the PLLA passes through its glass transition temperature. Before performing DLI experiments on this blend system, the blends were characterized by POM and the effect of PEO on the growth rate of PLLA spherulites was investigated.

The morphological diversity of the blends with different PEO weight fraction was observed under the polarized light optical microscope and is illustrated in Fig. 5. All of the samples were isothermally crystallized at 135 °C.

With low PEO weight fraction, the PLLA spherulites present smoother surface. With increasing PEO portion, the morphology becomes coarser. At the temperature examined, PEO is in the molten state, and is expelled outside the lamellae of PLLA. Thus, PLLA lamellae tend to be more opened by the amorphous PEO component. The last image in Fig. 5 corresponding to pure PEO is totally black, and this is because PEO is above its melting temperature at this temperature. As a first approximation, judging by the above images, it would seem that the effect of increasing PEO on the morphology of the PLLA spherulite is indeed to open up the texture of the spherulite, in keeping with the expectation stated earlier.
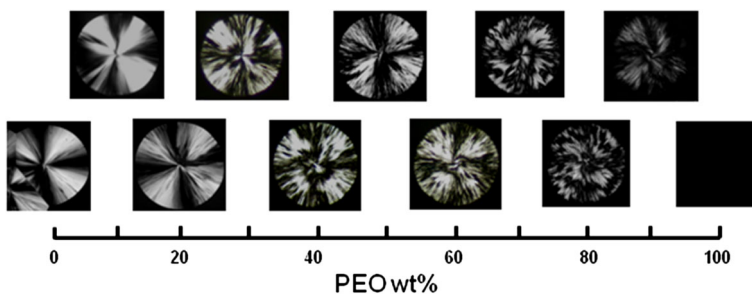

Fig. 5 Polarized light optical micrographs of individual spherulites in PEO/PLLA blends crystallized at 135 °C showing different morphologies. (Mag.) = ×200

Figure 6 shows the growth rates of PLLA spherulites in the PEO/PLLA blends of different PEO composition and includes that of pure PLLA data for comparison. The data are spread over two graphs in an attempt to make a clearer presentation [odd wt% PEO blends in (a) and even in (b)].

The steeper slope of the blend curves compared to that of the pure sample indicates that PLLA spherulitic growth rates in blends increase with undercooling at a greater rate than that of the pure PLLA. In short, for most blends, PLLA spherulites are growing at a faster rate when PEO is present. The enhanced growth rate can be attributed to the properties of PEO: the low T_g of PEO provides increased chain mobility in the blend melts. Consequently, the growth rate of PLLA increases due to the decrease of activation energy of diffusion [16]. As PEO fraction increases, the increasing mobility is counteracted finally by the dilution effect of PEO chains on the crystallizable PLLA. At very large PEO compositions, as in the
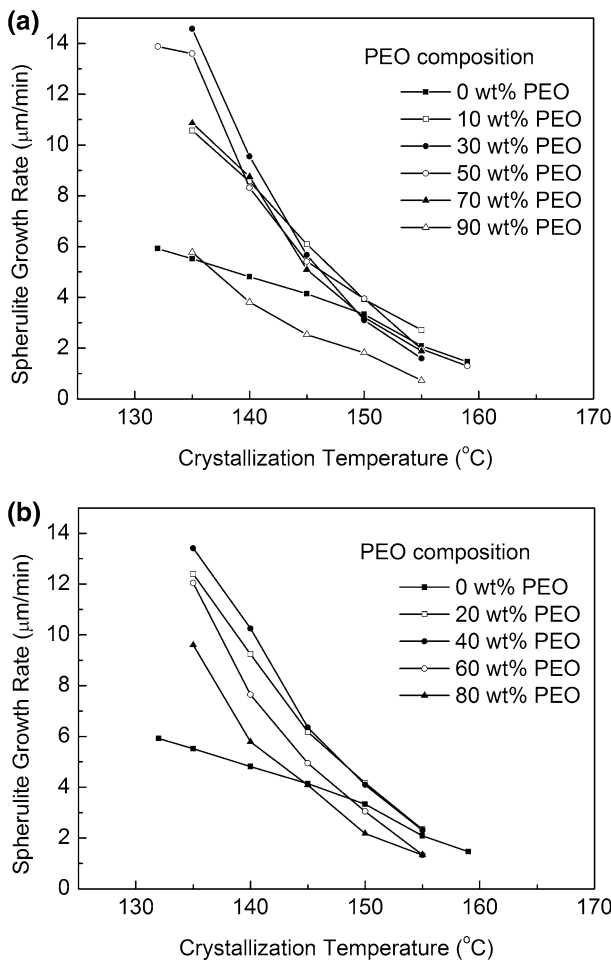

Fig. 6 Radial growth rates of PLLA spherulites in blends with PEO of different compositions as a function of crystallization temperature. *Lines* are drawn for the ease of presentation but not denote a fit

PEO/PLLA 90/10 blend, the dilution effect is so great that PLLA growth rate is finally retarded relative to the pure PLLA.

On measuring the growth rates of PLLA with various PEO compositions, it was observed in the microscope that, regardless of the amount of PEO present in the blend, the spherulites of PLLA are still able to grow to impingement, given enough time at the isothermal condition, even when PEO is present in 90 wt%. This observation prompted the question: where is PEO? PLLA spherulites impinged with straight and thin lines of impingement, therefore, eliminating the possibility of inter-spherulitic PEO. Thus, PEO has to be between the lamellae of the PLLA (i.e., inter-lamellar region). At a given T_c, the PEO might be 'trapped' at different levels of the structural hierarchy of the PLLA spherulite. It does not necessarily suggest that there will be a linear response to the location of the PEO in PLLA with composition. It might be the case that, for a range of blend compositions, the location of the PEO in the PLLA remains constant.

DLI experiments were performed on the PEO/PLLA 50/50 blend and the results are shown in Fig. 7. The samples were crystallized as open-face thin films at 130 °C prior to enzyme solution degradation. The samples were then washed with deionized water and dried with N_2 before characterization. Water took away PEO in the blend, and its imprint could denote where PEO was. By analyzing the thin film sample, the effect of PEO on the crystallization and degradation behavior of PLLA could be further studied.

Similar to that of the pure PLLA, the DLI profiles of the blend presented a gradual increase upon heating. The most outstanding feature in this group of DLI data is the offset difference in the range of 140 and 170 °C among the plots. The sample which had not been degraded apparently melts sooner than the rest of the samples. This result might be attributed to two possible actions: (1) enzyme etching; or (2) PEO diffusion. In the first case, during the period of enzymatic degradation, the amorphous section and
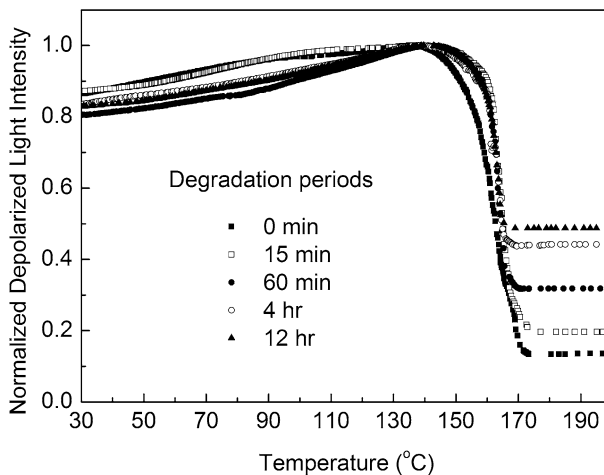

Fig. 7 DLI heating profiles (10 °C/min) of 50/50 wt% PEO/PLLA blends following enzymatic degradation for different periods according to legend. All samples crystallized as open-face thin films at 130 °C for 80 min prior to enzymatic degradation. Deionized water was used to wash the sample before dried with N_2. The *error bar* is within the size of the data points

crystals with less perfection have been eaten up and removed, and thus has developed more order and, therefore, a higher T_c. In the second case, the PEO fraction makes the blend more hydrophilic, resulting in faster absorption of a considerate amount of water from the aqueous-buffered enzyme solution, so it was easier for the removal of PEO. Thus, PEO becomes diffused away from the blend and causes the increase in the T_c of the thin film sample. In Fig. 7, all of the blend samples, as a group, show an onset to melting (indicated by the initial drop in light intensity) at a higher temperature than that of the non-degraded sample. The increased T_c of the blends as a group (either because of by (1) or (2) above) accounts for this slightly higher melting temperature.

There was no DLI drop at the melting temperature of PEO, indicating a complete wash away of PEO component. It was observed that only the light intensity plot of the 15-min run (130–150 °C) differs from the rest of the plots of the blend samples, indicating that the enzyme was effective only after 15-min degradation. The results are in agreement with what has been reported that a faster initial degradation in PEO/PLLA blend [17–19] or in copolymer [20, 21] than in pure PLLA.

With half of the polymer blend comprised PEO, the PLLA crystals showed coarser texture (Fig. 5). At the longest degradation time applied in this set of experiments (i.e., 12 h), the remained DLI signals after melting were extraordinarily high. It is in compliance with what was proposed in the former text. PEO facilitated the degradation of PLLA in the more opened-up lamellae, resulting in much shorter PLLA chain segments. A resultant wide distribution of polymer chain length might lead to a higher degree of phase separation, resulting in the high remained DLI.

To further investigate how PEO facilitated the degradation of PLLA, how PEO was accommodated in its blend with PLLA needs to be examined. Some research groups have used electron microscope images for direct observation upon removing PEO [22, 23]. In this study, where and how PEO would crystallize under DLI is analyzed as supplementary evidence.

Two-step crystallization experiments were done on the blend samples with the second step monitored by DLI. After an isothermal crystallization treatment ($T_c = 100$ °C) to crystallize the PLLA component, the temperature was further lowered to crystallize the PEO component. DLI was used to follow the crystallization of the PEO. The results of the cool from 100 to 30 °C are shown in Fig. 8 for each of the blend samples investigated.

Upon looking at the results in Fig. 8, it is immediately apparent that the results fall into three groups of DLI profiles. The three different crystallization DLI profiles may be signaling three types of crystallization, specifically, three types of ordering (or not) of the PEO component inside the PEO/PLLA blend.

The crystallization of PEO during the cool to 30 °C is apparent by the sudden increase in light intensity in almost all of the plots. Almost no change in signal was detected for the 10 and 20 wt% samples. It is important to note that the y-axis showed the relative changes of light signals. Therefore, even this group appeared to have the highest y values, it did not indicate the highest values of absolute light intensity, but the smallest DLI changes. In this group of two plots, it can be postulated that the PEO is not able to crystallize. The apparent inability of PEO to crystallize in these blends can be attributed to its dispersion throughout the inter-lamellar regions of the major component, PLLA spherulites. It is reasonable to suggest that PLLA is able to reject any highly mobile PEO from entering into the
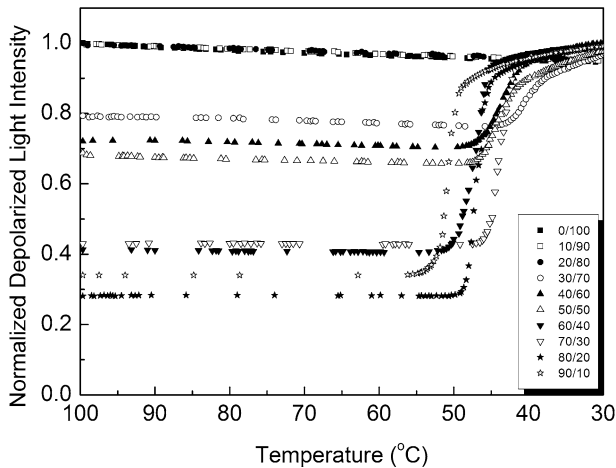
Fig. 8 DLI cooling profiles (10 °C/min) of PEO/PLLA blends of different compositions showing PEO crystallization. Compositions are listed as PEO/PLLA (wt/wt). All samples crystallized as open-face thin films at 100 °C for 15 min prior to cooling. The *error bar* is within the size of the data points

low entropy crystalline lamellae. The relatively small amount PEO can get trapped between two relatively rough fold surfaces of neighboring PLLA lamellae. This observation at least is in agreement with what Younes and Cohn [24] have reported. They stated that over the whole range of compositions of PEO/PLLA blend, the component is not able to crystallize with a less than 20 % weight ratio. Younes and Cohn also indicated that the amorphous phase of PLLA might accommodate some of PEO molecules, so that the crystallization of PEO is sufficiently hindered by PLLA.

The DLI crystallization profiles of the 30, 40 and 50 wt% PEO/PLLA blends are similar and standout as a unique second group of blends. Here again, the similar profiles are an indication of a similar internal arrangement of the PEO in the blend. The small but significant increase in intensity for each of these blends in this second group is an indication that PEO is able to crystallize and do so in a similar fashion. It is proposed that PEO still finds itself rejected and trapped onto the inter-lamellar regions of the PLLA spherulite. In this group, however, there is more PEO in this region than merely a layer that it accommodated by the fold surface of the PLLA lamellae. In addition to this layer, there is more PEO and it can, therefore, attain some order upon cooling in this confined space, but not enough to form spherulites of its own.

The greatest increase in intensity upon cooling was found for the third group of blends, those with >50 wt% PEO. It is suggested that the now major component PEO is able to form its own spherulites (evidenced by POM, not shown) among the existing, rather open PLLA spherulites. The PEO might have ultimately been trapped between PLLA fibrils instead of lamellae. It may be able to crystallize in a similarly open spherulitic structure that ultimately forms an inter-digitating network of spherulites with the existing PLLA in the final solid. It is also important to note that the onset to PEO crystallization is earlier in this third group of blends. This

indicates that the PEO is present as a more dense component in which nucleation is more likely to occur at a higher temperature and, therefore, appears earlier during this analysis.

Once each of the blends in Fig. 8 had remained at 30 °C for 5 min, the heater was applied to the sample and the subsequent heating DLI profile was acquired for each of the blend samples. The results are plotted in Fig. 9. The results in this figure maintain the distinction of the three blend groups, each showing a unique thermal behavior upon melting.

There are two regions of general intensity drop, attributed to the melting of PEO and then PLLA, respectively. In the melting experiment, the 10 and 20 wt% PEO blend samples maintain similar behavior as group (1) blends. Neither of these samples displayed a melting light intensity loss at about 60 °C for the PEO component, which is in keeping with the lack of any observable crystallization of PEO in this group in Fig. 8.

The 30, 40 and 50 w% PEO blend samples maintained their distinction in this experiment as group (2) blends. In this group, the melting of PEO is indeed observed at about 60 °C, as expected and followed by the melting of PLLA in the second drop in intensity. It is interesting to point out that the 50 wt% PEO blend sample intensity profile appears above that of the 40 wt% PEO blend sample, reinforcing the idea that these samples are divided into groups and do not have a linear-type response in their profiles to the change composition.

Finally, the group (3) blends, in which the PEO is the major component, all possess similar light intensity–melting profiles, unique as a group to the other group profiles. This group shows the greatest decrease in intensity upon PEO melting. As stated earlier, the intensity signals have been normalized so that the y-axis can be
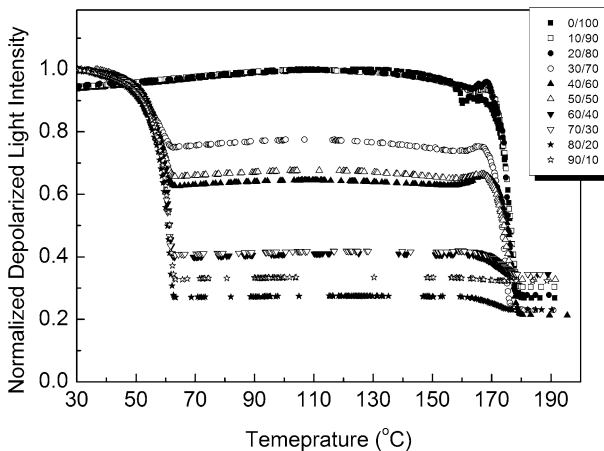

Fig. 9 DLI heating profiles (10 °C/min) of PEO/PLLA blends of different composition. Compositions are listed as PEO/PLLA (wt/wt). All samples crystallized as open-face thin films at 100 °C for 15 min, then cooled to 30 °C at 10 °C/min for 5 min prior to the acquired DLI heating. The *error bar* is within the size of the data points

read as a relative increase in intensity, it is thus seen that the last group has the greatest crystallinity in the PEO component.

It is interesting to see the feature on the second drop in intensity for each of the samples in Fig. 9. Just before final melting of the PLLA component above 170 °C, there is a bump in the profile, or, a small increase in intensity just before the final loss. In fact, in the 0 wt% PEO sample, it can be seen that the sample starts to melt, as indicated by a small decrease in intensity, before the subsequent increase in intensity. In this sample, therefore, the PLLA is able to partially melt, partially recrystallize, and finally melt. This is a clear manifestation of the metastable nature of the polymer, and the small exothermic dip is unique to the 0 wt% blend sample. The reordering feature manifest by the 'bump' before final melting is present on all of the profiles of the group (1) and (2) blends. There is no apparent reordering of the PLLA in at least the 80 and 90 wt% PEO samples of the group (3) blend samples in which the PLLA is the minor component.

To summarize, three groups of PEO/PLLA blends have been distinguished: (1) 10–20 wt% PEO; (2) 30–50 wt% PEO; and (3) 60–90 wt% PEO. With less than 20 wt% of PEO, and without any significant phase separation process, there is not enough PEO in any local area to develop into any sort of folded-chain structure. Rather, it is most likely accommodated by the relatively rough fold surface of the PLLA lamellae. PEO is able to form ordered structures in the two groups, (2) and (3), with the PEO assigned to the intra-spherulitic space (i.e., inter-lamellar).

Conclusions

DLI was used to study the crystallization and degradation behavior of PLLA and its blends with PEO. DLI is sensitive to study the degree of order in polymer thin film samples. It could also imply the degree of degradation to some extent. Combination of DLI and in situ observation of polymer morphology under POM is a useful way for understanding the phase behavior of systems of interest.

Blending PEO with PLLA increases the growth rate of the PLLA spherulites, depending on two factors—mobility and dilution. For the DLI cooling profiles, three groups have been identified: (1) 10–20 wt% PEO cannot form any order in the binary blend; (2) 30–50 wt% PEO is able to form some order but not enough to develop spherulitic crystals; (3) 60–90 wt% PEO can form spherulites. The DLI melting profiles completely support this proposal.

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