Crystallization behavior in miscible blends of poly(ε-caprolactone) and poly(hexylene adipate) with similar thermal properties studied by time-resolved Fourier transform infrared spectroscopy

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Funding information
The University of the South Pacific Research Committee, Grant/Award Number: F3106-FST12-001

Abstract
Melt crystallization behavior in miscible blends of poly(ε-caprolactone) and poly(hexylene adipate) was investigated by Differential Scanning Calorimetry, Polarized Optical Microscopy, Wide Angle X-Ray Diffraction and time resolved Fourier Transform Infrared Spectroscopy. Both polymers were highly crystalline, had similar thermal properties and exhibited negative birefringence. Fractional crystallization of PCL was observed in blends with <40 wt% PCL. Crystallization kinetics of the polyesters was investigated by monitoring the absorbance intensities of the bands at 841 and 911 cm\(^{-1}\) for PCL and PhAd respectively. Even though PCL exhibited a slow crystallization rate than PhAd at 47°C, simultaneous onsets of crystallization were found in all the blends. In blends with high PCL, the relative crystallinity values for both the polyesters were found to be coincidental while for blends with low PCL content the induction time of PCL shortened due to PhAd playing the role of nucleation agent. WAXD ruled out co-crystallization.

KEYWORDS
crystalline/crystalline blend, crystallization, FTIR, poly(hexylene adipate), poly(ε-caprolactone)

1 | INTRODUCTION

There has been a growing interest over the last decade to investigate crystalline/crystalline binary polymer blend systems because of the different morphological structures that can be obtained due to the crystallization of both polymers depending on the polymers’ thermal properties, crystallization condition, and blend composition.\(^\text{11–26}\) This makes it a challenge and interesting to understand the crystallization behavior of such systems when both components crystallize. The diversity of the crystalline morphological structures in these blend systems depends on the miscibility between the two components, the melting temperature difference (\(\Delta T_m\)), and the crystallization kinetics of the individual components and chemical structures.

Most miscible crystalline/crystalline blends reported so far in the literature can be categorized as those in which the individual component have; (1) large \(\Delta T_m\)\(^\text{11–8}\) or (2) small \(\Delta T_m\)\(^\text{9–23}\) In type (1) blends, sequential crystallization has been observed where the high \(T_m\) component crystallizes first even when its content was low in the blend. The low \(T_m\) component either remained amorphous in the interspherulitic, interlamellar, and interfibrillar of the crystallized component or nucleated and crystallized in these confinements at large supercooling. This latter phenomenon is known as fractional crystallization. The mechanism of fractional crystallization is well-documented in the literature.\(^\text{1,3,7}\) Type (ii) blends exhibit simultaneous crystallization of both the components, sometimes resulting in co-crystallization\(^\text{24–26}\) and the formation of interpenetrating spherulites.\(^\text{7–15}\) Co-crystallization in miscible crystalline/crystalline blends is rare and limited to polymer pairs with similar chemical structures. During co-crystallization, both the components can exist inside a lamella, in separate lamellas inside a fibril, in separate fibrils inside a spherulite, or in separate spherulites\(^\text{27}\) and can be easily traceable by infrared spectroscopy where the
crystalline bands of both the components grow simultaneously. However, this technique can also give misleading conclusions especially when two components crystallize simultaneously but in separate lamella. Thus, co-crystallization should be confirmed through X-ray diffraction method by observing the formation of new crystals that contain both the polymer chains.

Recently, the crystallization behavior in a miscible crystalline/crystalline blend of poly(ethylene suberate) (PESub)/poly(ethylene oxide) (PEO) with similar thermal properties was reported\(^\text{[13]}\) to exhibit fractional crystallization behavior in both components when it was the minor in the blend at large supercooling. Similarly, blends of poly(L-lactic acid) PLLA and poly(oxyethylene) (POM) also having similar thermal but different crystallization kinetics\(^\text{[14]}\) have shown a combination of behaviors observed among several polymer blends with different \(\Delta T_m\) such as simultaneous or separate crystallization, depending on the blend composition and \(T_c\).

Few literature are available on blend systems with similar \(T_m\)\(^\text{[1,10–18,20]}\) because it is rare to find such a combination. The crystallization behavior in these blend systems has been investigated mostly by thermal and microscopic techniques.

Thus, it would be interesting to investigate new miscible crystalline/crystalline blend systems with similar thermal properties and fast crystallization kinetics, but different chemical structures and the possibility of co-crystallization.

In this study, poly(\(\epsilon\)-caprolactone) (PCL) and poly(hexylene adipate) (PhAd) were chosen to be blended because of similar thermal properties, fast crystallization kinetics and different chemical structures. Both polymers are semicrystalline, linear polyesters with great potential as biomaterials. The chemical structures are shown in Figure 1. To the best of our knowledge based on the literature review, there have been no reports on the crystallization behavior studies of PCL/PhAd crystalline/crystalline blend system.

In this article, the crystallization behavior of PCL and PhAd and its blends were investigated using time-resolved Fourier transform infrared spectroscopy (FTIR). The results from this investigation will contribute to a better understanding of the crystallization behavior in miscible crystalline/crystalline polymer blends with similar thermal properties and fast crystallization kinetics.

## EXPERIMENTAL

### 2.1 Materials

PCL was purchased from Aldrich Chemicals and used without further purification. The \(M_w\) of PCL determined by GPC was 30 300. PhAd was synthesized\(^\text{[28]}\) with \(M_w\) of 37 400 and given to our group by Prof Hideki Abe. Analytical grade chloroform (CHCl\(_3\)) was used as the solvent and was distilled before use.

### 2.2 Sample preparation

Different mass ratios of PCL and PhAd were dissolved in chloroform to form blends with varying compositions to obtain 100/0, 80/20, 60/40, 50/50, 40/60, 20/80, and 0/100 where the first value represents the PCL. The solvent was evaporated at room temperature at first and further dried in vacuum at 30 °C for several days to remove the residual solvent completely. The dried samples were used for thermal, optical, and infrared analysis.

### 2.3 Differential scanning calorimetry

The thermal behavior of the blends was characterized by differential scanning calorimetry (DSC) (Perkin Elmer DSC Pyris 6). About 8 mg of the sample was sealed in an aluminum pan and subjected to different thermal treatment. The samples were first scanned at a heating rate of 10 °C min\(^{-1}\) up to 90 °C and kept for 5 minutes to remove thermal history then cooled nonisothermally at a cooling rate of 5 °C min\(^{-1}\). The minimum of the exothermic peak was taken as the \(T_c\). For the determination of the glass-transition temperature (\(T_g\)), the samples were scanned from –90 to 25 °C at a heating rate of 10 °C min\(^{-1}\) and the midpoint of the transition was taken as the \(T_g\). For isothermal treatment, the samples were cooled from the melt at a cooling rate of 50 °C min\(^{-1}\) to 47 °C and kept at this temperature for 6 hours before cooling it nonisothermally at 5 °C min\(^{-1}\) to ambient temperature.

### 2.4 Wide angle X-ray diffraction

Wide angle X-ray diffraction (WAXD) experiments were performed on isothermally crystallized samples using a RINT-2000 system (Rigaku Corp.) with Cu K\(\alpha\) radiation (\(\lambda = 0.15418\) nm) operating at 40 kV and 40 mA. The intensity of the X-ray was measured in a symmetrical transmission mode within the range of 2θ from 2° to 45° using a scintillation counter at a scanning of 1° min\(^{-1}\).

### 2.5 Infrared spectroscopy

Infrared spectra of the neat polymers and the blends were obtained using a Perkin-Elmer 100 Spectrum FTIR at 2 cm\(^{-1}\) resolution. The samples were melted on a NaCl window and sandwiched between another NaCl window to obtain a thin film. The films were thin enough to follow Lambert Beer’s law. Ten scans were averaged for each spectrum recorded. A high temperature sample holder designed by our group\(^\text{[29]}\) was used to obtain the spectra in the melt state. For isothermal crystallization, the samples on the NaCl windows were cooled from the melt to the preset \(T_c\) in the high temperature cell.

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**FIGURE 1** The chemical structure of poly(\(\epsilon\)-caprolactone), A, and poly(hexylene adipate), B
Time-dependent infrared spectra of the blends were obtained during isothermal crystallization. Recording of the spectra was stopped when the absorbance intensity of the crystalline bands of the two polyesters became constant. Mathematical manipulation of the data was carried out by the instrument’s software.

2.6 | Microscopic infrared spectroscopy

FTIR (JASCO, FT/IR-6300) equipped with a polarized infrared microscope (JASCO, IRT-3000) was used to determine the absorbance spectra of the spherulite of the 60/40 blend sample crystallized at 47°C. The signal/noise ratio of the spectra was minimized by taking a square aperture with an area of 100 × 100 μm² at the pupil plane of the microscope and the sample chamber was purged with nitrogen gas. The measured spectrum was normalized.

2.7 | Polarized optical microscopy

The spherulite morphology of the neat polymers and the blends was observed under a crossed polarized optical microscope equipped with a first-order retardation plate, a Nikon digital camera and a hot-stage. The samples were melted on a microscopic glass slide at 90°C, kept for 5 minutes to erase thermal history, before covering with a cover slip. The samples were then transferred to the hot stage preset at 47°C and isothermally crystallized. The spherulite morphology in the melt and at different times during isothermal crystallization was recorded.

3 | RESULTS AND DISCUSSION

3.1 | Thermal properties

The melting thermograms of the neat polymers and of the blends obtained at a heating rate of 10°C min⁻¹ after isothermally crystallizing at 47°C are shown in Figure 2A. In neat PCL, a single melting endotherm was observed which shifted to higher temperatures when crystallized at higher Tₐ’s indicating an increase in the lamellar thickness. In PhAd, a broad single melting endotherm was observed despite being crystallized at different temperatures with no change in the Tₐ. This broad melting endotherm can be explained on the basis of melting-recrystallization and remelting process, which is usually present in many linear biodegradable polyesters. In the blends, a single melting endotherm was also observed indicating both the polymers melted simultaneously. Figure 2B shows the enlarged heating thermogram at lower temperatures to capture the Tₐ of the polyesters and the blends. The Tₐ of PCL was determined to be −63°C, comparable to reported values while for PhAd was determined to be...
Although the $T_g$ of the two polyesters were very close, the blends showed a composition dependent $T_g$ indicating the blends are miscible. The nonisothermal cooling thermograms of the neat polymers and the blends obtained at a cooling rate of 5°C min$^{-1}$ from the melt after erasing thermal history are shown in Figure 2C. The $T_c$ of PCL and PhAd was located at 30 and 42°C, respectively. The blends exhibited a composition dependent crystallization exotherm intermediate between the exotherms of the neat polymers, which originated from the simultaneous crystallization of the two polymers except for blends with low PCL content (40/60 and 20/80) which showed two crystallization exotherms. The crystallization exotherm at low temperature had been enlarged for clarity and given in Figure 2D. This low temperature crystallization exotherm is attributed to the fractional crystallization of PCL, that is, the fraction of PCL that had remained in the interlam ella region at higher crystallization temperature and crystallized at a lower temperature. Our results are in agreement with other blends exhibiting fractional crystallization.\[16-23]\] Interestingly, the fractional crystallization behavior was not observed in blends with PhAd being the minor component. Observations from this blend system are different from the reported PEO/PESub miscible system.\[13\] This observation is probably due to the difference in the crystallization kinetics of the two polyesters at 47°C, PhAd having a faster rate than PCL and therefore, all the PhAd was able to crystallize even though it was the minor component in the blend. The thermal properties of neat PCL, PhAd, and the blends obtained from DSC are given in Table 1. The degree of crystallinity ($X_c$) was calculated to be 66% for both polymers using $\Delta H$ of 139.5 J/g\[35\] and 155 J/g\[36\] the enthalpy of fusion for 100% crystalline PCL and PhAd, respectively.

The interesting question that arises is how the two polyesters crystallized within the common exothermic peak, which was impossible to study with the current DSC technique. To explore further, time-resolved infrared spectroscopy was used.

### 3.2 | POM observation

Figure 3A-F shows the morphology of the blends in the melt and semicrystalline states. Figure 3A shows the micrograph of the 60/40 blend in the melt. A homogenous phase in the melt indicated the two polyesters were not phase separated. Figure 3B-F shows the spherulites of neat PCL, the blends and PhAd obtained at 47°C. PCL showed large spherulites with negative birefringent while PhAd also showed negative birefringent, but the spherulite size was small (Figure 3F). This observation in PhAd is because the nucleation density and crystallization rate of PhAd were higher at 47°C. In the blends, morphologically similar type of spherulites was observed, which made it difficult to distinguish the two polymers individually by POM and study the crystallization process.

### 3.3 | Wide angle X-ray diffraction

Crystal structure modification in polyester blends due to transesterification can be identified by WAXD pattern. Figure 4 shows the WAXD pattern for PCL, PhAd, and 20/80 blend isothermally crystallized at 47°C. For PCL, the characteristic peaks were observed at angles $2\theta = 21.4^\circ$ and $23.8^\circ$, which were assigned to the (100) and (200) planes, respectively.\[37\] For PhAd, the peaks were found to be at $21.3^\circ$ and $23.9^\circ$ assigned to the 220 and 040 planes, respectively.\[38\] PCL and PhAd have similar diffraction pattern and the peaks overlap.
in the one-dimensional diffraction pattern. The diffraction pattern of the blend showed no new peak indicating the absence of the formation of new crystal, ruling out co-crystallization.

### 3.4 | Time-resolved Fourier transform spectroscopy

FTIR has been successful in studying the crystallization process [27, 39–42] in polymers because the IR absorption bands associated with the crystalline conformation are easily detectable because these bands increase with time as crystallization progresses. For many blend systems, this technique of analysis becomes a challenge due to the overlap of bands from the two components. However, for this blend system, fortunately, one of the crystalline band from the two polymers did not overlap and therefore did not require spectral manipulation.

#### 3.4.1 | Infrared peak characterization of PCL and PhAd

Figure 5 shows the infrared spectra of PCL in the semicrystalline state obtained at 30°C and amorphous state obtained at 90°C. Several distinctive changes in the IR band positions were observed between the two phases.

During melt crystallization, the absorption intensity of the bands at 1727, 1295, 1245, 1179, and 841 cm\(^{-1}\) increased and are attributed as the crystalline bands. The band at 1727 cm\(^{-1}\) is associated with the C=O stretching in the crystalline state that shifts to higher wavenumber, 1731 cm\(^{-1}\) in the amorphous state. The bands at 1295 and 1179 cm\(^{-1}\) are the stretching of C–O–C. Recently, through the use of gazing incidence reflection infrared (GIR-IR) spectroscopy, the band at 1245 cm\(^{-1}\) has been suggested to be the C–O–C stretching parallel to the C–C chain skeleton. [43] The band situated at 841 cm\(^{-1}\) is attributed to the CH\(_2\) rocking mode and was free from other overlapping bands.

In Figure 6, the IR spectra of PhAd in the semicrystalline (30°C) and amorphous states (90°C) are shown. Several bands at 1730, 971, 921, and 911 cm\(^{-1}\) increased in absorbance intensity with time and are associated with the crystalline phase. Like other polyesters, the band at 1730 cm\(^{-1}\) is due to the C=O stretching. The bands from 971 to 911 cm\(^{-1}\) are associated with the vibrations of the CH\(_2\) group and the band at 911 cm\(^{-1}\) is attributed to the CH\(_2\) stretching deformation. Comparing the IR spectra of the two polymers in the semicrystalline state, it was found that the bands at 841 and 911 cm\(^{-1}\) were unique to PCL and PhAd, respectively, and were independent of overlaps from other bands from the two polyesters.

#### 3.4.2 | Time-resolved infrared spectroscopy of the blends during isothermal crystallization

The impartialness of the 841 and 911 cm\(^{-1}\) bands in the blends made it possible to follow the crystallization process of the two components in the blends directly by monitoring the absorbance intensity of the two bands with time. The emergence time of the two bands depended on the blend composition and the T\(_{c}\). Table 2 shows the emergence of the two bands with respect to blend ratio and the T\(_{c}\). All the blend ratios showed simultaneous emergence of the two bands at temperatures 47°C and below.

The time-dependent IR spectra of the 60/40 blend at 47°C cooled from the melt are shown in Figure 7. For conciseness, the IR spectra at temperatures below 47°C are not shown, which gave similar results to that observed at 47°C. The crystallization behavior of the two polyesters in the blends was investigated at this T\(_{c}\).

To understand the crystallization kinetics of the two polyesters in the blends, the relative degree of crystallinity, \(X(v,t)\) at time, \(t\) was determined according to Equation 1

\[
X(v,t) = \frac{A(v,t) - A(v,\min)}{A(v,\max) - A(v,\min)}
\]

where \(A(v,t)\) is the absorbance at wavenumber \(v\) (\(v = 911\) or 841 cm\(^{-1}\)) at time, \(t\). \(A(v,\min)\) and \(A(v,\max)\) are the absorbance of the two bands at the start of crystallization (amorphous) and at completion of crystallization, respectively. Figure 8A-F shows the time dependence relative crystallinity, \(X(v,t)\) of the neat polymers and in the blends during isothermal crystallization at 47°C. Furthermore, the crystallization half time, \(t_{1/2}\) was estimated from the plots in the linear region when \(X(v,t)\) was around 0.5 according to Equation 2.

\[
t_{1/2} = \frac{(0.5 - b_{t_{1/2}} / m_{t_{1/2}}) \times (A(v,\max) - A(v,\min)) + A(v,\min)}{b_{t_{1/2}}} - b_{t_{1/2}} / m_{t_{1/2}}
\]

The data selected from the linear region of the \(A(v,t)\) versus \(t\) graph were plotted and using the linear least squares method, the slope, \(m_{t_{1/2}}\), and the intercept, \(b_{t_{1/2}}\) were obtained from the linear fit.
The $t_{1/2}$ of the two polymers in the blend has been labeled in Figure 8A-F.

For PCL (Figure 8A) and PhAd (Figure 8B), the $t_{1/2}$ was determined to be 71.2 and 2.3 minutes, respectively, indicating that PhAd had a faster crystallization rate at 47°C. The induction time in PCL was around 60 minutes, which resulted in a long $t_{1/2}$. In the blends, the induction time and $t_{1/2}$ depended on the blend composition. The induction time for PCL decreased as the amount of PhAd increased indicating that the nucleation in the blends is initiated and driven by PhAd.

For the 80/20 blend (Figure 8C), the relative crystallinities determined using the bands at 841 and 911 cm$^{-1}$ showed the same time dependence, indicating that both the polymers crystallized simultaneously. However, the relative crystallinities started to increase after a lapse of 60 minutes from the time the sample was brought to 47°C and took almost 300 minutes for the relative crystallinities of the polyesters to become constant. The $t_{1/2}$ of the two polymers was found to be 106 minutes. The nucleation and crystallization of both polyesters were delayed. The diluting effect of PCL on PhAd significantly retarded the nucleation and crystallization rate. The probable mechanism is, the PCL chains (present in large amount) entrapped the PhAd chains in the melt and did not allow the PhAd chains to crystallize. Once the nucleation was initiated, both the polyesters started crystallizing simultaneously. The simultaneous emergence of the crystalline bands of the two polymers indicated the possibility that PhAd co-crystallized with PCL. However, this is ruled out because the WAXD results indicated the absence of any new crystals formed for this blend ratio. Therefore, the two polyesters formed separate lamellar.

For the 60/40 blend (Figure 8D), the crystallization induction time was reduced when compared to the 80/20 blend. The crystalline bands from both polyesters appeared simultaneously during the initial stages of crystallization up to 10 minutes, after which the 911 cm$^{-1}$ band grew faster than the 841 cm$^{-1}$ band. The two polyesters maintained their respective crystallization rates during the crystallization process.

For the 40/60 blend (Figure 8E) and 20/80 blend (Figure 8F) as the PCL content decreased in the blends, the induction period shortened and the crystallization rate of PhAd increased much faster than PCL. The shortening of the induction period of PCL indicates that PhAd was acting as the nucleating agent for PCL. The crystallization behavior can be explained on the basis of the difference in the crystallization rates of the two polyesters. During the initial stages of crystallization, both polymers crystallized simultaneously. As crystallization progressed, due to the difference in the chain kinetics of the two polyesters at 47°C and the decreasing content of PCL in the blends, the PCL chains got excluded from the growing front of the PhAd lamella and got entrapped between the PhAd lamellae. Due to the high $T_c$ combined with restricted chain mobility of PCL in the inter-lamellar region of PhAd, the PCL lamellae was formed slowly due to the retardation of PCL crystallization rate. Some of the PCL remained amorphous between the PCL and PhAd lamellae, which crystallized at low temperatures. This proposed mechanism is supported by DSC measurements where two exothermic peaks were observed for 40/60 and 20/80 blends in the cooling scan of DSC and are shown in Figure 2D. The exothermic peak around 30°C incorporated the crystallization of both polymers and the exothermic peak at lower temperature was due to the crystallization of PCL entrapped in the inter-lamellar regions as shown in Figure 2C,D. Similar behavior has been reported for PESub/PEO blend.[13]

Furthermore, microscopic infrared spectroscopy was also performed on one of the spherulite in the 60/40 blend. Due to the increased noise in the signals, the first derivative of the absorbance was calculated and plotted against wavenumber as shown in Figure 9. The presence of sharp changes at 1010, 973, 911, 841, 791, and

![FIGURE 6](image6.png)  FTIR spectra of PhAd in the crystalline (30°C) and amorphous phase (90°C). The band at 911 cm$^{-1}$ is the crystalline band unique to PhAd

![FIGURE 7](image7.png)  Time-dependent FTIR spectra of the 60/40 blend at 47°C cooled from the melt

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This table shows the blend ratios and the crystallization temperature showing simultaneous emergence of the bands, ●, and time delayed, ○, of the two crystalline bands from the two polyesters.
718 cm$^{-1}$ in the range of 1050 to 700 cm$^{-1}$ was observed in the derivative plot. The interest was to examine the presence of the bands at 911 and 841 cm$^{-1}$ which indicated the presence of both polymers in the same spherulite. This result is in good agreement with the suggested mechanism explained earlier.

This is an interesting blend system having similar thermal properties and fast crystallization kinetics but different chemical structures. Time-dependent FTIR spectroscopy can mistakenly indicate that blends with low PhAd content is capable of showing co-crystallization when both the crystalline peaks emerge simultaneously during crystallization. However, WAXD results showed diffraction peaks for PCL and PhAd crystals confirming simultaneous crystallization and ruling out co-crystallization. Nonetheless, time-dependent FTIR spectroscopy has shown to be a useful technique to track the mechanism of crystallization for blend systems that have common $T_m$ and $T_c$.

## 4 | CONCLUSION

Crystalline/crystalline blends of biodegradable polyesters, PCL and PhAd were prepared through solution casting and investigated the crystallization behavior using differential scanning calorimetry (DSC), polarized optical microscopy (OPM), and FTIR spectroscopy. Both polymers had similar thermal and morphological properties. Blends of these two polyesters were miscible as a single composition dependent $T_g$ was observed. Thermal analysis showed all blend ratios to exhibit a common $T_m$ and $T_c$ except for blends with low PCL content which exhibited two $T_c$'s. The high temperature $T_c$ is a result of the simultaneous crystallization of both polymers, whereas the low temperature $T_c$ is attributed to the fractional crystallization of PCL.

The crystallization kinetics of the polyesters was investigated using time-resolved infrared spectroscopy. The absorbance intensities of the crystalline bands at 841 cm$^{-1}$ and 911 cm$^{-1}$ for PCL and PhAd, respectively, was monitored with time and the crystallization behavior of the two polymers in the blend varied according to $T_c$ and blend composition.

FTIR results showed simultaneous onsets of crystallization for all the blends examined in this study, although PCL showed a slow crystallization rate than PhAd. Simultaneous appearance of the crystalline bands from the two polyesters was seen throughout the crystallization process in blends with low PhAd content (80/20). Blends with
increasing PhAd content, phase segregation followed after simultaneous crystallization and the induction period of PCL was significantly shortened because PhAd played a role of the nucleation agent. WAXD did not show any new diffraction peaks in the blend ruling out the formation of new crystal form, thus excluding co-crystallization.

The concurrent emergence of the two bands indicates that both polyesters crystallized simultaneously but in separate lamella. With increasing PhAd content in the blend combined with faster crystallization kinetics, PhAd lamella formed much faster than PCL forcing PCL to undergo fractional crystallization.

ACKNOWLEDGMENT
The authors would like to thank Prof. Hideki Abe for providing the PhAd and Mr. Sanjay Singh of the Engineering School for helping in designing the high temperature FTIR sample holder. The University of the South Pacific Research Committee for funding this research (F3106-FST12-001).

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REFERENCES

How to cite this article: Rohindra D, Lata R, Kuboyama K, Ougizawa T. Crystallization behavior in miscible blends of poly(ε-caprolactone) and poly(hexylene adipate) with similar thermal properties studied by time-resolved Fourier transform infrared spectroscopy. Polymer Crystallization. 2018;1–8. https://doi.org/10.1002/pcr2.10037