

Structural Changes in Poly(trimethylene adipate) and Poly(trimethylene succinate) During Melt Crystallization Studied Using In Situ Infrared Spectroscopy

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Abstract

This paper investigates the structural changes occurring in poly(trimethylene adipate) (PTAd) and poly(trimethylene succinate) (PTSu) during melt crystallization using differential scanning calorimetry (DSC) and in situ Fourier transform infrared (FT-IR) spectroscopy. Cooling thermograms revealed that PTAd had a faster crystallization rate than PTSu. Infrared (IR) bands of the two polyesters were assigned by correlating with the IR bands of polymers containing the trimethylene and the diacid segments. The bands at 1478, 1459, 1393, and 1364 cm^{-1} in PTAd and 1475, 1459, 1393, and 1361 cm^{-1} in PTSu were designated to the CH_2 of the trimethylene segment. Changes in the IR band absorbance intensities of the CH_2 and the $\text{C}-\text{O}-\text{C}$ groups were monitored with time during melt crystallization. Structural changes of the trimethylene and diacid segments of PTAd occurred synchronously, while in PTSu the two segments changed sequentially. Normalized band intensities showed a time lag between the trimethylene and succinic acid segments. The acid segment showed a faster change compared to the trimethylene segment. Fourier transform infrared spectroscopy is shown to be a useful technique to study conformational changes during crystallization in polymers.

Keywords

Poly(trimethylene adipate), poly(trimethylene succinate), mid-Fourier transform infrared spectroscopy, mid-FT-IR, crystallization

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Introduction

Interest in investigating aliphatic polyesters in the last decade has increased because of its biodegradable nature. As the usage of these polyesters increases for different applications in the near future, it is of fundamental importance, both from an academic and an industrial perspective, to understand the structure–property relationship when subjected to different conditions.^{1–7} The structural changes that occur in crystalline polymers during the crystallization process are of general interest because the physical and mechanical properties strongly depend on the crystalline phase. Reports on the structure–property relationship in polymers containing 1,3-propanediol have been lacking. This was mainly because of the unavailability of the 1,3-propanediol monomer due to the high cost involved in its manufacture.^{6,8,9} After the success of Shell and DuPont in producing this monomer at a cheaper cost, more polymers are now available in the market.

Among the polymers containing the trimethylene group, many investigations have concentrated on poly(trimethylene terephthalate) (PTT),^{6,8,10–20} an engineering thermoplastic belonging to the family of aromatic polyesters.

Previous investigations on PTT have mainly focused on the effect of the odd number of carbon atoms in the methylene segment on the melting and crystallization behavior^{6,12–16} under different conditions. It was found

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that PTT showed unique properties compared with its PET and PBT counterpart in the homologous series owing to the odd number of methylene group in the alkyne segment.^{21,22} Structural changes in PTT during crystallization have been studied by infrared (IR) spectroscopy.^{8,11,19} Fourier transform infrared (FT-IR) spectroscopy has been successful in studying the conformational changes in crystalline polymers during crystallization^{1–5,8,11,19,23–35} because the IR absorption bands originate due to the different functional moieties in the polymer chain and their conformation are sensitive to temperature. As the temperature decreases during melt crystallization, the crystalline bands emerge and the absorbance increases synchronously. Major changes in PTT were found to occur in the trimethylene segment during crystallization.^{8,11,19} Furthermore, conformational changes observed during melt and cold crystallization revealed that the CH₂ segments of the melt-crystallized samples were more stable than cold crystallized.¹⁹

Recently, poly(trimethylene succinate) (PTSu) and poly(trimethylene adipate) (PTAd) have also been made available commercially. These polyesters are biodegradable, semi-crystalline, linear polyesters with the monomer chemical structure given in Fig. 1. Like PTT, both PTAd and PTSu contain a trimethylene group in the monomer unit. However, they differ in the diacid segment that makes PTAd and PTSu more flexible compared with PTT where the presence of the phenyl ring provides restriction. It would be interesting to compare the structural changes taking place in these polyesters during melt crystallization. Based on our literature search, most of the works on these two polyesters are on the biodegradation rate, blends, and drug release properties^{36–45} reported by the Bikirais et al. research group. The purpose of this research was to assign some characteristic IR bands of PTAd and PTSu in the crystalline and amorphous phases and study the structural changes occurring in these polyesters during melt crystallization through in situ FT-IR spectroscopy. There are no reports on the IR band assignments of the two polyesters and the conformational arrangement of the chains in the crystalline and amorphous states based on our literature search. To assign the IR bands originating from the trimethylene segment, the IR spectra of PTT was used. For the assignment of the adipic acid segment, IR spectra of polymers in the adipic acid homologous series of poly(butylene adipate) (PEAd), poly(tetramethylene adipate) (PBAd), poly(hexamethylene adipate) (PHAd), and adipic acid were used while for succinic acid; poly(ethylene

succinate) (PESu), poly(butylene succinate) (PBSu), poly(hexamethylene succinate) (PHSu), and succinic acid were used. It is anticipated that the in situ FT-IR technique will contribute to the better understanding of the structural changes occurring in the polymer chains of PTAd and PTSu during melt crystallization.

Experimental

Materials

The PTAd was purchased from Scientific Polymer Products, Inc. and the PTSu was purchased from Sigma Aldrich in granular form. The M_w of PTAd and PTSu were 3800 and 9500, respectively. The polymers were used as received without further purification.

Differential Scanning Calorimetry

Thermograms of the polyesters were obtained using a Perkin Elmer Pyris 6 differential scanning calorimeter (DSC). Temperature calibration was performed with an indium standard. About 8 mg of the sample was sealed in an aluminum pan and scanned from 0 °C to 80 °C at a heating rate of 10 °C min⁻¹ and kept at this temperature for 2 min to remove thermal history before cooling was done from 80 °C to -35 °C at different cooling rates from 10 °C to 0.5 °C min⁻¹. All scans were performed under nitrogen gas flow of 20 mL min⁻¹. The exothermic peak was taken as the crystallization temperature (T_c). Isothermal crystallization was performed by rapidly cooling (80 °C min⁻¹) the sample from the melt to the preset T_c and held for 6 h. The melting temperature (T_m) of these samples was determined by scanning at different heating rates. The endothermic peak was taken as the T_m .

Infrared Spectroscopy

Infrared spectra were obtained using a Perkin Elmer Spectrum 1000 FT-IR spectrometer at a resolution of 2 cm⁻¹. Calibration was carried out using polystyrene standard. Ten scans were averaged for each spectrum. Difference spectrum was obtained by the instrument's software.

For isothermal melt crystallization analysis of the polyesters, a high temperature sample holder to accommodate

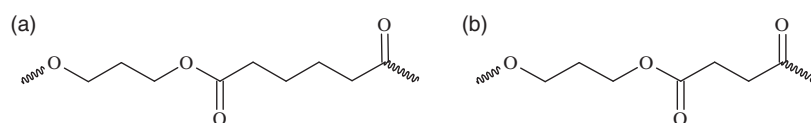


Figure 1. Monomer structure of (a) PTAd and (b) PTSu.

the NaCl window containing the polymer sample was designed by our group, as shown in Fig. 2. This holder was connected to a temperature controller (Graseby Specac) and the temperature of the holder was controlled precisely to $\pm 0.5^\circ\text{C}$. The polyester was melted and smeared as a thin film between two NaCl windows. During isothermal crystallization, the IR spectrum was recorded at preset time intervals until the absorbance intensity of the bands became constant.

Results and Discussion

Thermal Behavior

Fig. 3 shows the DSC cooling thermograms of PTAd and PTSu at various cooling rates. For PTAd, the crystallization exotherm appeared between 6°C to -6°C for cooling rates of 1.5°C to 5°C min^{-1} , respectively. The decrease in T_c with increasing cooling rate is due to thermal lag. No exothermic peak was observed for PTSu even at the slowest cooling rate of $0.5^\circ\text{C min}^{-1}$, indicating no crystallization. It has been reported that these polyesters have the slowest crystallization rate in the homologous series exhibiting the odd–even effect.³⁶ Samples isothermally crystallized below 30°C showed double melting peaks in both the polyesters when heated at a rate of $10^\circ\text{C min}^{-1}$ as shown in Fig. 4a and b. In PTAd, the T_m of the first endotherm was detected at 27°C for the sample crystallized at 18°C . This T_m shifted to higher values with increasing T_c while the T_m (40°C) of the second endothermic peak remained unchanged. Similarly, for PTSu two melting endotherms were observed, the T_m of the lower endotherm was around 30°C while the T_m of the higher endotherm was around 42°C . The behavior of the endothermic peaks in PTSu for samples crystallized with increasing T_c also showed similar trend to that of PTAd. Detailed analysis of the multiple melting peaks of PTAd⁴⁰ and PTSu³⁶ have been reported using thermal and wide-angle X-ray scattering (WAXS) techniques and the origin of the multiple melting peaks has been associated with the melting, recrystallization, and remelting process and not due to different crystal modifications. This observation is consistent with the

melt–recrystallization process as seen in other polyesters.^{46–48} Using samples crystallized at 30°C where a single melting peak was observed in the DSC thermogram the degree of crystallinity of PTSu was determined to be 34% using the enthalpy of fusion for a perfect crystal, (ΔH°), of 140 J/g ³⁶ and for PTAd was calculated to be 43% using the ΔH° of 134 J/g .⁴⁰

Infrared Spectroscopy of the Polyesters

The IR spectra of PTAd and PTSu obtained during isothermal crystallization at 20°C quenched from the melt are shown in Fig. 5a and b, respectively. A comparison of the crystalline and amorphous spectra indicated several distinctive bands that can be attributed to the two different phases. During crystallization, it is suggested that the polymer chains change their conformation in order to stack uniformly in lamellar crystals. To interpret the IR spectra in terms of changes in the conformation of the polymer chains during crystallization, correct band assignment is important. According to Fig. 1, the monomer unit of the

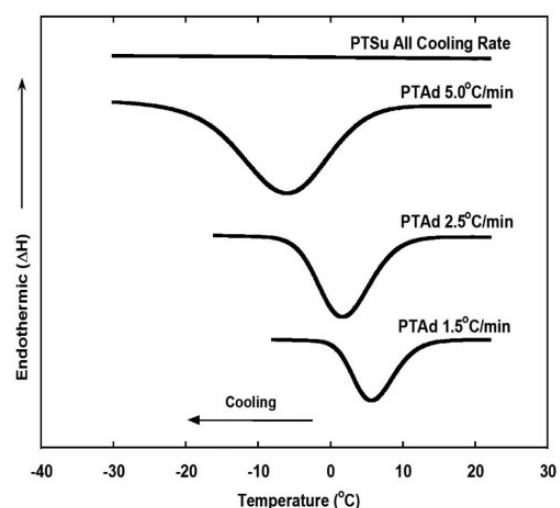


Figure 3. The crystallization exotherms of PTAd and PTSu at different cooling rates.

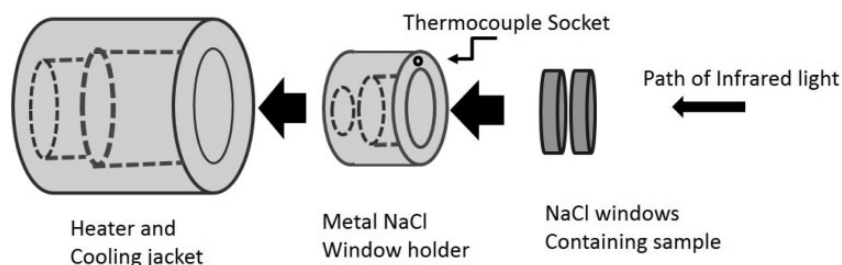


Figure 2. The different components of the high temperature cell.

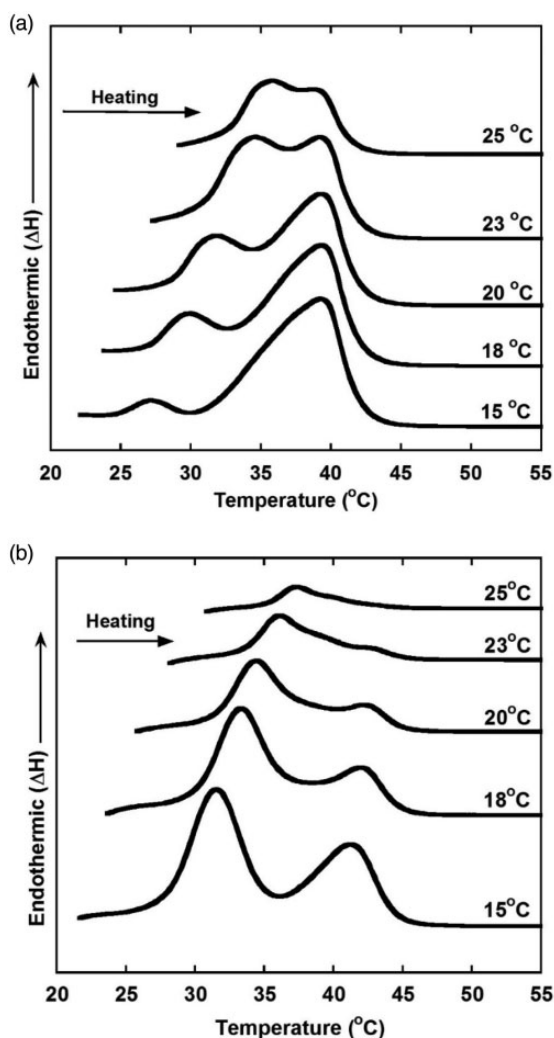


Figure 4. The melting thermograms of (a) PTAd and (b) PTSu at a heating rate of 10 °C/min for samples isothermally crystallized at various temperatures.

polyesters contains two segments, the trimethylene segment and the diacid segment, and both the segments are connected by the carbonyl group ($\text{C}=\text{O}$). The band around 1700 cm^{-1} is the stretching of the carbonyl group in the two different phases. In the crystalline phase, the carbonyl band is at lower wavenumber compared with the amorphous phase. Furthermore, the second derivative of the carbonyl band in the crystalline phase revealed the presence of two inverted peaks, a small one at higher wavenumber and a large one at lower wavenumber confirming the semi-crystalline state of the polymer after crystallization. During crystallization, it was noted that the change in the absorbance intensity of the $\text{C}=\text{O}$ band was not that significant compared to the shift in the wavenumber. Therefore, the change in the absorbance intensity of $\text{C}=\text{O}$ was not able to provide information on the type of structural changes taking place in the two segments because the carbonyl

group being at the junction of the two segments. Hence, this band is not used in our analysis.

A shoulder peak at 1686 cm^{-1} in the crystalline state is indicative of some interactions involving the carbonyl band during packing of the polymer chains in the lamellar. The mid-IR region ($1700\text{--}600\text{ cm}^{-1}$) was used in this study to investigate the structural changes in the polyesters during melt crystallization. Each polyester will be discussed separately.

Mid-Infrared Region of PTAd

Fig. 5a shows the IR spectra of PTAd during melt crystallization. The vibrational bands were assigned to the adipic acid segment and the trimethylene segment. The bands at 1469 , 1419 , 1176 , 919 , and 733 cm^{-1} were characteristic of the adipic acid segment and were verified by observing the spectra of adipic acid, PEAd, PHAd, and PHAd. The bands at 1478 , 1459 , 1392 , 1373 , 1364 , and 948 cm^{-1} were characteristic of the trimethylene segment. These assignments were found to be in good agreement with the band positions observed in PTT⁸ and PTSu (next section).

Due to the unavailability of the chain conformation of PTAd in the crystalline state in the literature, in this study we have attempted to assign the conformation of the trimethylene segment by correlating the IR bands associated with the trimethylene segment conformation from PTT.

The band at 1459 cm^{-1} present in the amorphous phase is attributed to the *trans* CH_2 bending of the trimethylene segment. This band splits into a doublet, 1478 and 1469 cm^{-1} in the crystalline state. The former band is assigned as the *gauche* CH_2 bending of the trimethylene segment while the 1469 cm^{-1} is that of the adipic acid segment. However, the band at 1459 cm^{-1} still remains as a weak band in the crystalline phase, which suggests that the *trans* conformation is not completely lost.

The band at 1363 cm^{-1} in the amorphous phase, attributed to the *gauche* CH_2 wagging conformation, becomes sharper and shifts to 1373 cm^{-1} in the crystalline phase. Similarly, the band at 948 cm^{-1} , attributed to the *gauche* CH_2 conformation of the trimethylene segment,⁸ which has a weak absorbance intensity in the amorphous phase, becomes strong in the crystalline phase. According to Fig. 5a, the bands at 1261 , 973 , 948 , 919 , 906 , and 733 cm^{-1} , absent in the amorphous phase but became sharper and increased in absorbance intensity with increasing crystallization time, are sensitive to the crystalline conformation. The assignment of the PTAd IR bands is given in Table I.

Mid-Infrared Region of PTSu

The mid-IR region of PTSu is given in Fig. 5b. The bands associated with the succinic acid segment appeared at 1412 ,

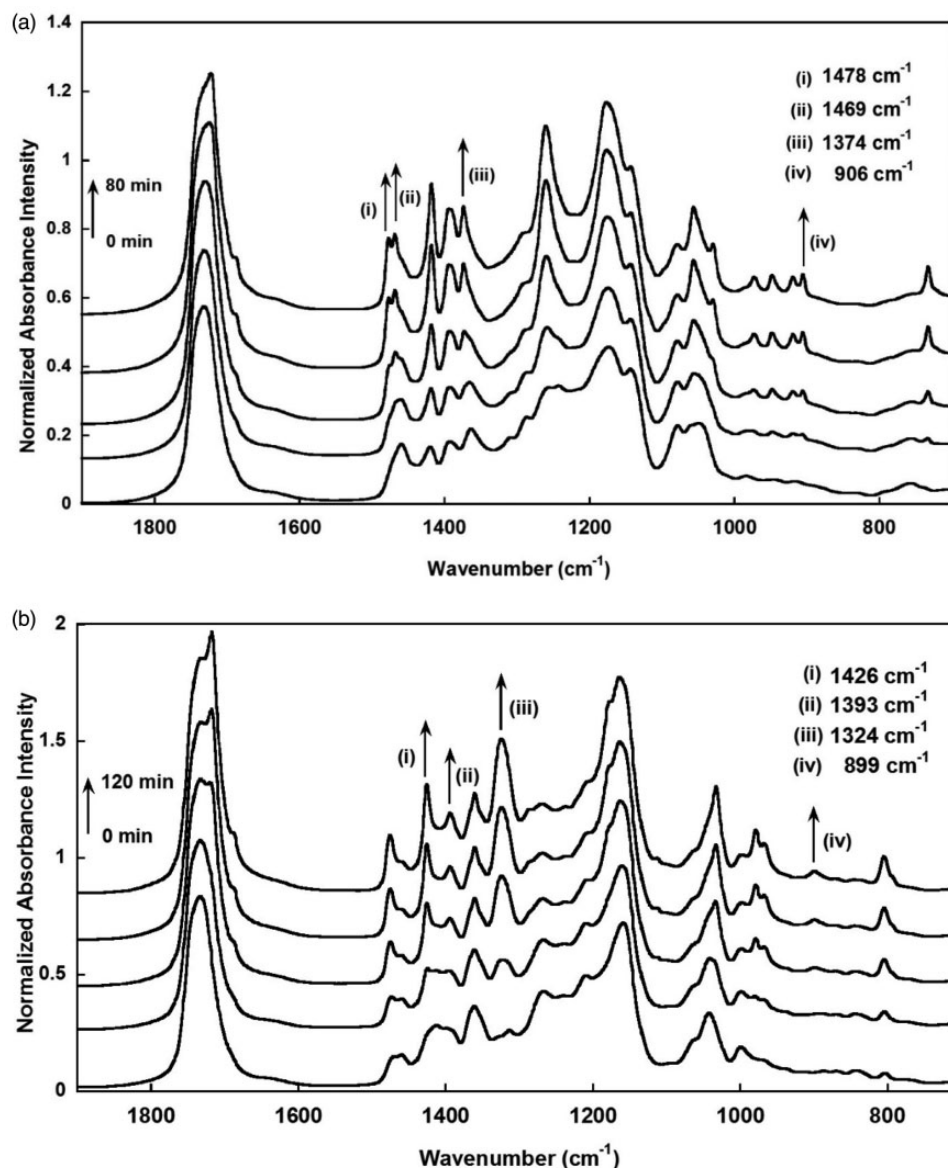


Figure 5. In situ FT-IR measurements for isothermal crystallization at 20 °C in the region 700–1900 cm^{-1} . (a) PTAd and (b) PTSu.

1313, 886, and 803 cm^{-1} in the amorphous phase and shifted to 1425, 1324, 899, and 804 cm^{-1} in the crystalline phase, respectively. These bands were confirmed by correlating the IR bands of succinic acid, PESu, PBSu, and PHSu.

Like PTAd, there is no literature on the conformation of the PTSu chains in the crystalline state. Therefore, IR bands in PTT corresponding to the trimethylene segment were used in the assignment of the trimethylene segment in PTSu. The band at 1459 cm^{-1} that appeared as a medium strength band in the amorphous phase became weak in the crystalline phase; this band is assigned to the *trans* CH_2 bending of the trimethylene segment. In the crystalline phase, this band shifted to 1475 cm^{-1} and the absorbance intensity became stronger and sharper, which is assigned to

the *gauche* conformation of the CH_2 bending of the trimethylene segment.

Furthermore, the band at 1398 cm^{-1} appeared as a weak shoulder in the amorphous phase became sharper and moved to lower wavenumber of 1393 cm^{-1} in the crystalline phase. This band is attributed to the *trans* CH_2 wagging of the trimethylene segment. The band at 1360 cm^{-1} that showed a similar behavior to that of PTAd in the amorphous phase, attributed to the *gauche* CH_2 wagging conformation of the trimethylene segment became a medium-sized band in the crystalline phase retaining the same wavenumber.

Bands at 1426, 1393, 1324, 979, and 899 cm^{-1} showed an increase in band absorbance intensity with crystallization

Table 1. Assignment of infrared absorption bands of PTAd in the amorphous and crystalline states.

Amorphous (cm ⁻¹)	Crystalline (cm ⁻¹)	Band assignment
1732 (s)	1722 (s)	C=O stretching.
	1478 (m)	<i>gauche</i> CH ₂ bending (trimethylene segment)
	1469 (m)	CH ₂ bending (adipic segment) [CH ₂ -(C=O)]
1459 (s)		<i>trans</i> CH ₂ bending (trimethylene segment)
1419 (m)	1418 (s)	CH ₂ bending (adipic segment)
1392 (m)	1393 (s)	<i>trans</i> CH ₂ wagging (trimethylene segment)
	1374 (m)	<i>gauche</i> CH ₂ wagging (trimethylene segment)
1364 (m)		<i>gauche</i> CH ₂ wagging (trimethylene segment)
	1261 (s)	
1049 (w)	1057	C–O/C–C stretch (adipic segment)
	973 (m)	C–O stretching [CH ₂ –O]
	948 (m)	<i>gauche</i> (trimethylene segment)
	919 (m)	CH ₂ Sketch deformation (adipic segment)
	906 (m)	CH ₂ Sketch deformation (adipic segment)
756 (w)	733 (s)	CH ₂ Sketch deformation (adipic segment)

time and are related to the crystalline phase. The band assignments are given in Table 2.

The behavior of the bands associated with the trimethylene segment in both PTAd and PTSu showed similar changes to that of PTT during crystallization. However, it should be noted that in PTT the trimethylene segment was the only flexible segment whereas in the polyesters studied in this work, both the trimethylene and the diacid segments were flexible. In order to evaluate how the conformation of the two segments in the polyesters were changing during crystallization, the kinetic study was performed.

Crystallization Kinetics

The bands that showed increasing absorbance intensity with crystallization time were used for kinetic studies. For PTAd, bands at 1478, 1374, 1057, and 906 cm⁻¹ and PTSu bands at 1426, 1324, 1393, and 899 cm⁻¹ were selected. These bands were associated with the two different segments. The absorbance intensity of each band was normalized to its maximum value that was measured after

Table 2. Assignment of infrared absorption bands of PTSu in the amorphous and crystalline states.

Amorphous (cm ⁻¹)	Crystalline (cm ⁻¹)	Band assignment
1733(s)	1716 (s)	C=O stretching
	1475 (s)	<i>gauche</i> CH ₂ bending (trimethylene segment)
1459 (m)		<i>trans</i> CH ₂ bending (trimethylene segment)
1412 (broad)	1426 (s)	CH ₂ bending (succinic acid segment). Also seen in PES
1393 (w)	1393 (m)	<i>trans</i> CH ₂ wagging (trimethylene segment)
1361 (s)	1361 (m)	<i>gauche</i> CH ₂ wagging (trimethylene segment)
1313 (w)	1324 (s)	CH ₂ wagging (succinic segment)
1159 (w)	1163	C–O stretching (succinic segment)
	1033 (s)	C–O stretching (trimethylene segment) also seen in PTT, PTAd
	979 (m)	C–O stretching [CH ₂ –O] (trimethylene segment) also seen in amorphous PTT
	899 (m)	CH ₂ wagging (trimethylene segment)
803 (m)	804 (s)	CH ₂ wagging (succinic segment)

the crystallization was completed. The normalized absorbance band intensity was plotted against the crystallization time that is given in Fig. 6a and b for PTAd and PTSu, respectively. The sigmoidal shape indicated the crystallization occurred by spherulite formation and was verified through microscopic observation (Supplemental Material). When crystallizing isothermally at 20 °C, the absorbance intensity of the crystalline bands of PTAd started to increase after 2 min from the time the sample was brought to this T_c and monitoring started. The absorbance intensities of the bands became constant around 80 min and remained almost unchanged thereafter. In contrast, the crystalline bands of PTSu emerged after 10 min and took almost 130 min for the absorbance intensity to become constant. However, the intensities of the bands were still increasing at a very slow pace till 190 min and did not change after that. In Fig. 6b, the plot is shown up to 130 min and the inset shows the plot on a shorter time scale to show the time lag from the two groups more explicitly. The crystallization process of PTSu was slow. This difference in the crystallization rate could be due to the difference in the molecular weight of the two polymers or the chain mobility of trimethylene segment and diacid segment in PTAd could be similar despite the size of the adipic segment being larger. In PTAd, the normalized

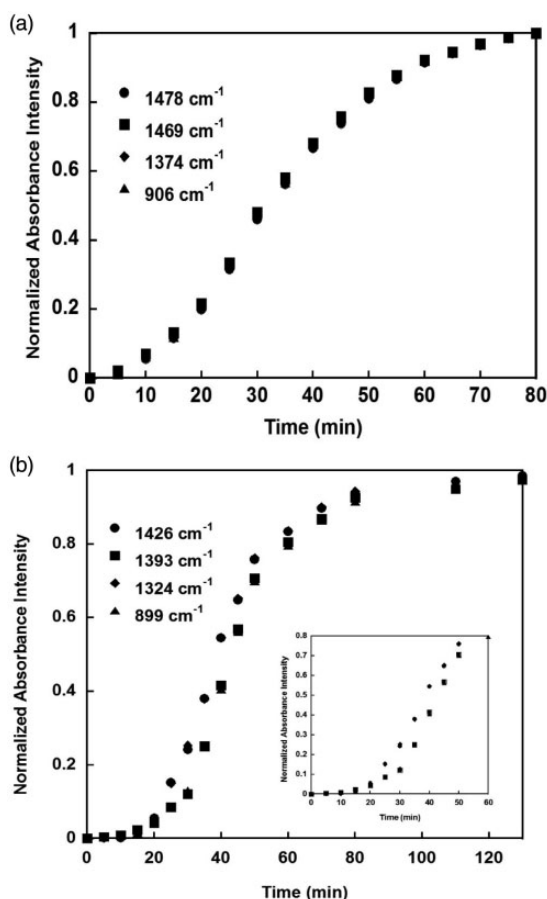


Figure 6. The normalized absorbance intensities of the crystalline bands against time (a) PTAd and (b) PTSu when isothermally crystallized at 20 °C. Insert (b) shows the enlarged version for better clarity of the time-lag between the two sets of data from the two segments.

absorbance intensity of the crystalline bands from both the diacid and the trimethylene segments overlapped, indicating that the structural changes of the two segments occurred simultaneously. This behavior is comparable to that reported for PBAd.⁴³ In contrast, the normalized band intensity of the crystalline bands in PTSu from the two segments did not overlap, suggesting that structural changes of the two segments occurred in sequence. Sequential structural behavior has been reported for PLLA²⁹ and PHB.³⁰ Further analysis of the normalized band intensities in PTSu showed that the bands at 1393 and 899 cm⁻¹ showed a time lag compared with that of peaks at 1426 and 1324 cm⁻¹. This indicated that the acid segment showed a faster change in conformation compared to the trimethylene segment. One of the suggested reasons for the slow crystallization rate of PTSu is the sequential structural change occurring in this polyester. The findings from this study shows that FT-IR is an important technique to study the conformational change occurring in polymers during crystallization.

Conclusion

In situ FT-IR spectroscopy and DSC were used to study the isothermal melt crystallization of PTAd and PTSu. The two polyesters showed significant difference in the crystallization rate, PTAd being fast and PTSu slow. Infrared band assignments of PTAd and PTSu were done using related polymers and adipic and succinic acids. The bands at 1478, 1459, 1393, 1374, 1364, and 948 cm⁻¹ in PTAd and the bands at 1475, 1459, 1393, 1361, and 899 cm⁻¹ in PTSu present in the amorphous and crystalline phases were designated to the CH₂ of the trimethylene segment. The bands at 1459 and 1393 cm⁻¹ are assigned to the *trans* conformation while the bands at 1478, 1475, 1374, 1364, 1361, and 948 cm⁻¹ to the *gauche* conformation. The normalized absorbance intensities of the bands associated with the trimethylene segment and the diacid segment against crystallization time showed that the structural changes in PTAd occurred cooperatively during crystallization while PTSu showed sequential changes. The succinic acid segment showed a faster structural change compared to the trimethylene segment. This time lag between the two groups may enlighten why the crystallization rate in PTSu is slow. This in situ FT-IR technique is shown to be a powerful tool to study conformational changes in slow crystallizing polymers.

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Conflict of Interest

The authors report there are no conflicts of interest.

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Supplemental Material

All supplemental material mentioned in the text, consisting of images of the sigmoidal shape indicating the crystallization occurrence with spherulite formation, is available in the online version of the journal.

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