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Utilization of Oligo(lactic acid) for Studies of Chain Conformation and Chain Packing in Poly(lactic acid)

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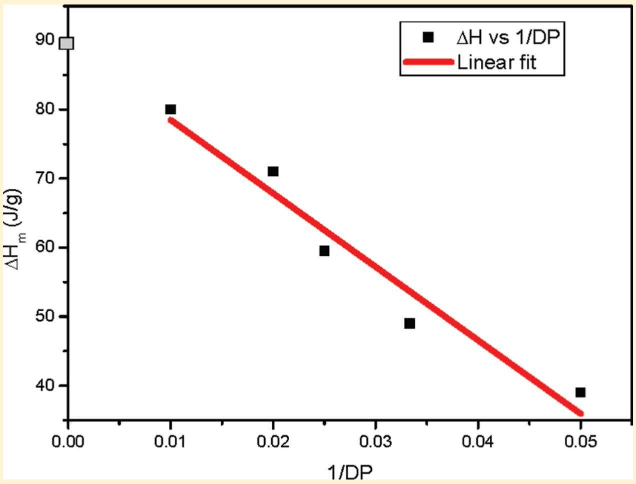
ABSTRACT: Based on a series of well-defined oligomers of lactic acid with different end-groups, calorimetric measurements and vibrational spectroscopic studies have been carried out to examine chain conformation and chain packing. These studies yielded data that are directly related to the models used for conformational analysis of both crystalline and amorphous PLA chains. The previously proposed rotational isomeric model dominated by the *trans*−*gauche*′−*trans* (*tg*′*t*) sequences has been confirmed. The linear relationship between enthalpy of fusion and reciprocal of lamellar thickness for chain-extended crystals was used to calculate the equilibrium enthalpy of melting of the α crystalline form of PLA and the value was found to be in close agreement with the previously proposed value of 93 J/g reported by Fischer. Using the same technique, the enthalpy of melting for the α′ phase has been determined to be 60 J/g. This confirms the value of 57 J/g reported by Kalish.



INTRODUCTION

With increasing focus on sustainability, research efforts to utilize polymeric materials from renewable resources are on the rise. Poly(lactic acid) (PLA) is one of the most widely utilized biodegradable thermoplastic polymers that is readily available from renewable resources. Applications for PLA include pharmaceutical formulations, drug delivery, sutures, orthopedics, tissue engineering, composites, textiles, and packaging.[1] First synthesized in 1932,[2] PLA was not utilized broadly as a thermoplastic because of the lack of suitable physical properties as compared to other polymers.[3] This situation changed when PLA began to be manufactured from renewable resources on a commercial scale. Since 1992, the starting monomers and dimers are being produced via a fermentation process, and the polymer is currently being produced commercially in a number of countries around the world.[2]

Despite the increasing commercial production, there are a number of fundamental structural features that are yet to be determined unambiguously. There are at least four polymorphic phases proposed for PLA: α, α′, β, and γ.[4] These polymorphic structures have specific chain conformation and crystalline packing.[5−9] The original rotational isomeric state (RIS) model used to describe PLA[10] has been refined over time, and a new model suggests a chain dominated by the *trans*−*gauche*′−*trans* (*tg*′*t*) conformation in either a 3_1 or a 10_3 helix with a higher characteristic ratio than previously reported.[11]

The literature values for the equilibrium enthalpy of melting, ΔH°_m, for PLA α crystalline phase vary over a wide range.[12−14] This uncertainty causes ambiguity in evaluation of the degree of crystallinity. Generally, the calculation of equilibrium melting enthalpy is correlated between crystalline dimensions measured by diffraction and heat flow for samples with differing degrees of crystallinity.[15] Because of the deviations in crystalline dimensions measured and the crystalline phase present, equilibrium enthalpy of melting values reported deviate considerably in various publications. The first reported value of ΔH°_m was 93 J/g using Flory's copolymer melting point depression expression.[12] Subsequently, Huang et al. reported a value of 100 J/g,[13] while Miyata and Masuko utilized the linear relationship between exothermic enthalpy change and density and reported a much higher value of 135 J/g.[14]

The uncertainties in structural parameters and heat of fusion are related to the fact that all previous studies have been carried out for semicrystalline PLA polymers containing amorphous regions as well as folds on crystalline lamellar surfaces. Structural reorganization commonly occurs during heating, i.e., lamellar thickening upon thermal annealing.[16] Equilibrium parameters are thus difficult to obtain since thermodynamic equilibrium is difficult to achieve. In this study, a series of oligomers of different molecular weights and end-groups were synthesized and fully characterized. In this systematic study, it is then possible to understand more fully the influence of short- and long-range interactions in determining chain conformation and packing and thus closely match simulation studies. Although chain end-groups

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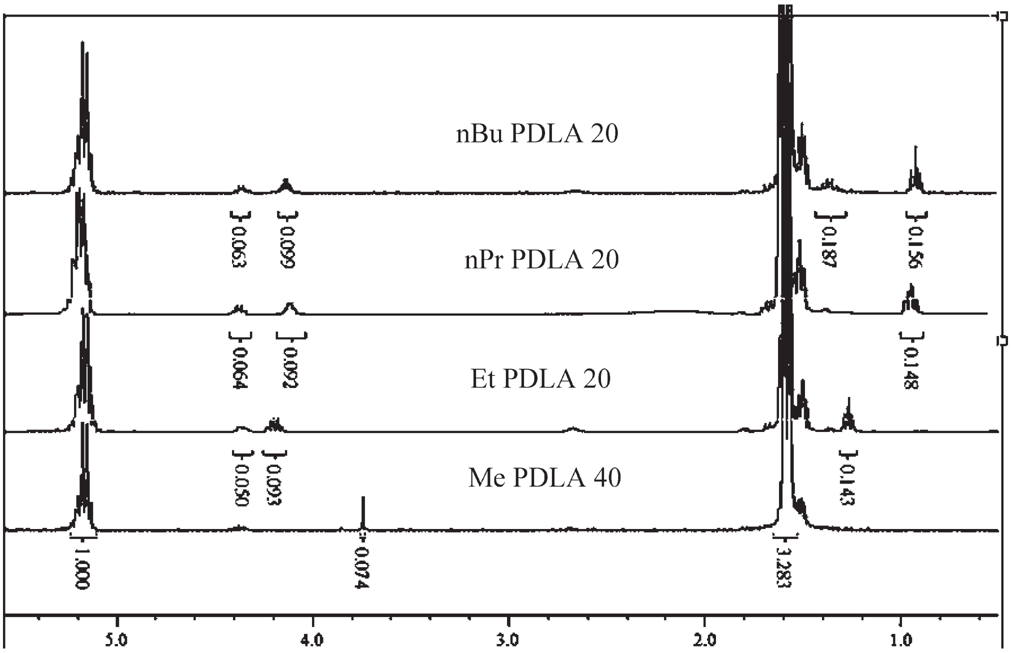

Figure 1. NMR spectra of Me PDLA 40, Et PDLA 20, nPr PDLA 20, and nBu PDLA 20.

can also perturb thermodynamic parameters, generally speaking, oligomers have a better-defined structure than polymers. Therefore, the study of oligomers is the best approach to understand equilibrium properties of the crystalline phase.

In this study, we present experimental data which confirms the stability of chain conformation of PLA as previously proposed.[5] Polarized Raman spectroscopy in conjunction with various simulation techniques has proven to be useful for investigating the chain conformation of both crystalline and disordered chains. The ambiguity in literature regarding the equilibrium enthalpy of melting of the α crystal form of PLA has also been clarified. The equilibrium melting enthalpy of the α and α′ crystalline phases was determined using the linear relationship between the enthalpy of fusion and the reciprocal of lamellar thickness of oligomer crystals.[17,18]

EXPERIMENTAL SECTION

Materials. D-Lactide ((3*R*-cis)-3,6-dimethyl-1,4-dioxane-2,5-dione) was obtained from Purac Biochem BV (Gorinchem, The Netherlands) and recrystallized from toluene before use. Stannous octoate (tin(II) bis(2-ethylhexanoate), $Sn(Oct)_2$, 96%) was purchased from Sigma Chemical Co. and was used as received. Methanol, ethanol, *n*-propanol, and *n*-butanol were purchased from Sigma Chemical Co.

Oligomer Synthesis. Lactic acid oligomers with varying molecular weights and different end-groups were synthesized using stannous octoate as catalyst and methanol, ethanol, *n*-propanol, and *n*-butanol as initiator. Oligomers with different degrees of polymerization were obtained by varying the monomer/initiator ratio. The procedure was as follows: 4 g of D-lactide along with the required amount of initiator was weighed into a vial and stirred at 130 °C under a nitrogen atmosphere until the lactide was molten. Subsequently, the required amount of stannous octoate catalyst, as a solution in ∼0.2 mL of toluene, was injected into the vial. Stirring was continued, and within 10 min the reaction mixture solidified. The temperature was raised to 160−180 °C depending on the targeted molecular weight, and stirring was continued. Total reaction time was 1 h. At the end of the reaction the oligomer was dissolved in dichloromethane, precipitated in hexane, and dried in vacuo. In general, the yield was greater than 90%. ^1H NMR (300 MHz) spectra were obtained on a Bruker DPX-300 NMR spectrometer. The spectra were measured in $CDCl_3$, and the chemical shifts were calibrated to the solvents' residual proton signal (^1H NMR signal: 7.26 ppm for $CDCl_3$). The molecular weight and dispersity were determined by GPC (Agilent). The oligomers were dissolved in chloroform at a concentration of 3 mg/mL, and the molecular weights measured were with respect to polystyrene standards.

Preparation of Amorphous Samples. Amorphous samples of the oligomers were prepared by melting the oligomers at 180−200 °C on a glass slide followed by quenching the oligomers in liquid nitrogen. The amorphous nature of the samples was confirmed by Raman spectroscopy.

Preparation of α and α′ Crystals. The α crystals were prepared by melting the oligomers on a glass slide (T_m of oligomers ranged from 115 to 173 °C depending on molecular weight) and cooling them to room temperature. This was followed by annealing the sample on a hot stage maintained at a temperature 20 °C below the melting point of the oligomers for 2 h. To prepare α′ crystals, the oligomers were melted on a hot stage and quenched in liquid nitrogen to obtain amorphous samples. These amorphous samples were then annealed on a hot stage at temperatures 90 °C below the melting point of the oligomers for 2 h. It was found that at annealing times greater than 1 h there was no further increase in the ΔH_m value. Therefore, 2 h was chosen as the annealing time to ensure that all samples crystallized completely. The crystallization procedure was performed in a nitrogen-protected atmosphere.

Raman Spectroscopy Analysis. Polarized Raman spectra were obtained by installing a polarization analyzer followed by a scrambler in the path of the backscattered beam from the sample. The polarized component was obtained by setting the analyzer polarization parallel to the polarization direction of the incident beam. The Raman instrument was manufactured by Horiba.

DSC Analysis. Thermal analysis was carried out with a TA Q100 differential scanning calorimeter (DSC) (TA Instruments) which was calibrated against an indium standard. For thermal analysis of the oligomers, the following program was used. In the first cycle the samples (5−10 mg) were heated at 10 °C min^{-1} to 190 °C and then cooled to −30 at 40 °C min^{-1}. In the second cycle the samples were heated at

Table 1. Molecular Weight Analysis of Oligomers

DP (theoretical)	DP (NMR)	M_n (g/mol) (NMR)	M_n (g/mol) (GPC)[a]	D
Me PDLA series				
10	13	940	2200	1.5
20	19	1400	4200	1.26
30	29	2100	5300	1.4
40	40	2900	6600	1.36
50	49	3500	8100	1.28
100	98	7100	13700	1.26
HMW			58699	1.5
Et PDLA series				
10	13	950	2300	1.34
20	22	1600	3500	1.42
40	41	3000	6400	1.29
nPr PDLA series				
20	22	1600	3100	1.19
40	43	3100	6000	1.4
nBu PDLA series				
20	22	1600	3200	1.26
40	38	2700	5200	1.36

[a] With respect to polystyrene standards.

10 °C min^{-1} to 190 °C. For thermal analysis of annealed samples, the annealed samples (5–10 mg) were run at a 10 °C min^{-1} heating ramp from −30 to 190 °C. All runs were performed in a nitrogen atmosphere (flow rate 50 mL min^{-1}).

■ RESULTS AND DISCUSSION

Characterization of Synthesized Oligomers. From previous studies it is known that stannous octoate is an initiator that gives high lactide conversion and a low racemization rate.[19−21] The NMR spectra obtained and integration values for all the resonances are shown in Figure 1. Table 1 shows the molecular weight characterization data obtained by ^{1}H NMR and GPC for oligomers with methyl (Me PDLA), ethyl (Et PDLA), *n*-propyl (nPr PDLA), and *n*-butyl (nBu PDLA) end-groups. In the case of Me PDLA oligomers, the degree of polymerization (DP) was calculated using the integration ratio of resonances for the lactide repeat unit methine protons (−CH quartet) and end-group methyl protons (−CH_3 singlet). For Et PDLA, nPr PDLA, and nBu PDLA oligomers the integration ratio of resonances due to the lactide repeat unit methine protons and end-group methyl protons (−CH_3 triplet) was used. The integration values of resonances due to end-group methylene protons (−CH_2 quartet in case of Et PDLA and −CH_2 multiplet in case of nPr PDLA and nBu PDLA) were found to be consistent with the integration values of end-group methyl protons. The DP values determined by ^{1}H NMR spectroscopy are in excellent agreement with the predicted values. The number-average molecular weights obtained by GPC are higher than those predicted. This is due to using polystyrene standards for GPC calibration and Mark−Houwink constants for these oligomers are not known. However, molecular weights determined by GPC show a monotonic increase in molecular weight as the degree of polymerization increases.

Chain Conformation Analysis. Polarized Raman spectra (symmetric modes) of amorphous samples of oligomers (Figure 2) were used to study the chain conformation of the oligomers so that the experimental data could be compared to simulated Raman spectra reported earlier.[5] The amorphous samples were used to understand the chain conformation in the disordered state for these oligo-PLA samples. The amorphous nature of these samples was verified by the presence of an infrared active vibration at 955 cm^{-1} as well as the absence of a crystallinity sensitive vibration at 922 cm^{-1}.[22,23] For a PLA repeat unit, the ester C−O bond is always in the trans conformation. The four favorable chain conformation states are *tt′t*, *tg′t*, *tt′g*, and *tg′g* based on theoretical and experimental treatments.[5,10,24] Experimental evidence suggests a disordered chain is dominated by ∼80% *tg′t* conformers. Following the analysis developed in previous studies, the 1000−1200 cm^{-1} region in the Raman spectra contains skeletal vibrations that are sensitive to these four favorable chain conformation states of PLA.[24] Figure 2 shows the polarized Raman spectra of amorphous oligo-PLA molecules ranging from 10 to 100 repeat units and with different end-groups. The 1128 cm^{-1} band is assigned to O_α−C stretching and C_α−H_α bending. The 1044 cm^{-1} band is assigned to C_α−C stretching and C_β−H_3 rocking.[25] Simulated spectra of a disorder PLA chain in this region can be seen in Figure 3. Details of the simulation method have been discussed previously.[5,24,25] Very good agreement between simulation and experiment has been observed for all oligo-PLA samples. The small frequency differences between the simulated and experimental spectra are due to the fact that all force fields are transferred from previous studies without further refinement.[25,26] This set of data shown in Figure 2 indicates an identical chain conformation distribution of PLA regardless of molecular weight or end-group. The Raman technique is not suitable for measuring chain stiffness. The spectra obtained, especially the isotropic spectra, indicate that the chain conformation of these PLA oligomers is dominated by the *tg′t* conformation, which is identical to that observed for polymeric samples. This confirms the RIS model proposed by Yang et al. This model predicts a characteristic ratio of 7−11. However, it should be mentioned that characteristic ratio cannot be the sole criteria for judging polymer chain rigidity.[27−29]

Analysis of α and α′ Crystals. As mentioned previously, the complexity of solid-state structure of PLA can be illustrated by the presence of polymorphic phases (α, α′, β, and γ) found to date.[4] The β and γ phases are difficult to obtain and are of little commercial value and thus have not been studied extensively. In contrast, α and α′ phases are generally found in the initial, intermediate, or the final state of various PLA products. Various studies have shown that the two states are extremely similar, differing slightly in the lateral spacing in the unit cell (both *a* and *b* axes).[30−33] The α crystal has the more compact unit cell which results in the development of stronger interchain interactions which enhances thermal properties and stability compared to the α′ crystal. Although the general features of the two crystalline states have been obtained, specific differences of the two phases remain. It is known that the α′ phase has distortion along the chain axis. The X-ray diffraction patterns obtained are generally of poor quality. As mentioned above, even the ΔH°_{m} for the more characterized α phase has a ∼40% uncertainty. This series of oligomers synthesized provide an unusual opportunity to further characterize the crystalline features of PLA.

Raman scattering has been used to characterize this series of oligomers. Since the chain conformation of oligomers is independent of the type of end-groups (Figure 2), we have focused on the methyl-terminated samples. Because of its small size, it is expected that chain packing will be the least perturbed by the methyl group. The difference in specific interchain interactions is

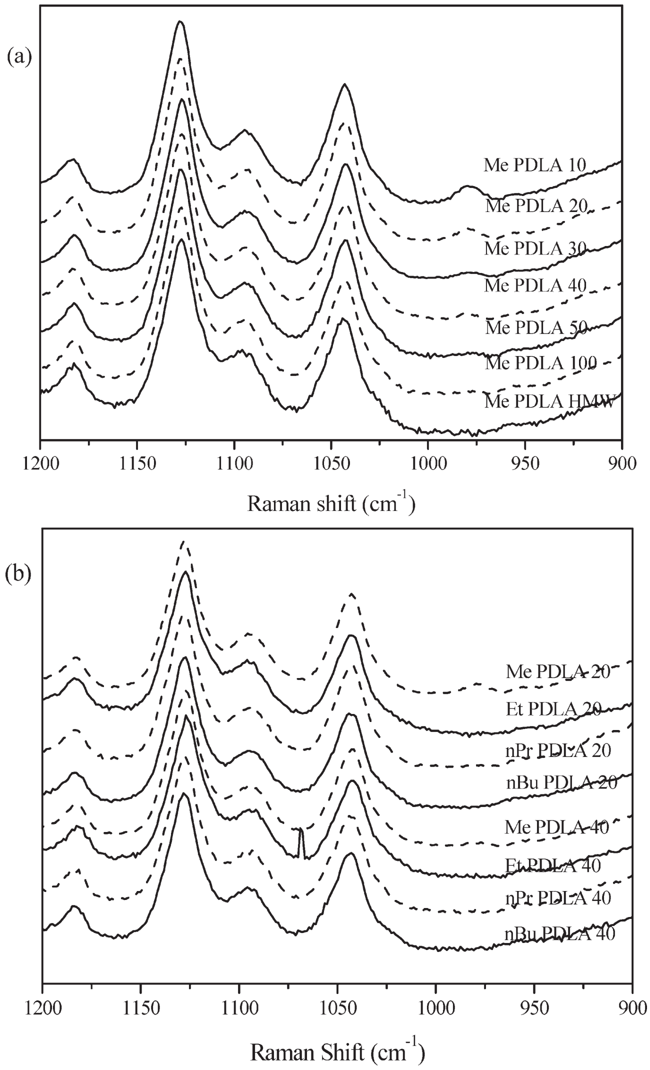

Figure 2. Polarized Raman spectra of amorphous samples from 1200 to 900 cm^{-1}: (a) methyl end-group oligomers with different DP (HMW: high molecular weight); (b) methyl, ethyl, *n*-propyl, and *n*-butyl end-group oligomers with DP 20 and 40.

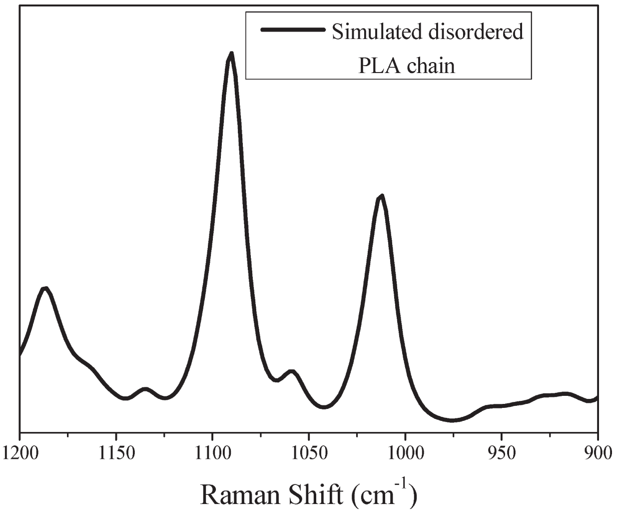

Figure 3. Simulated disordered PLA chain.

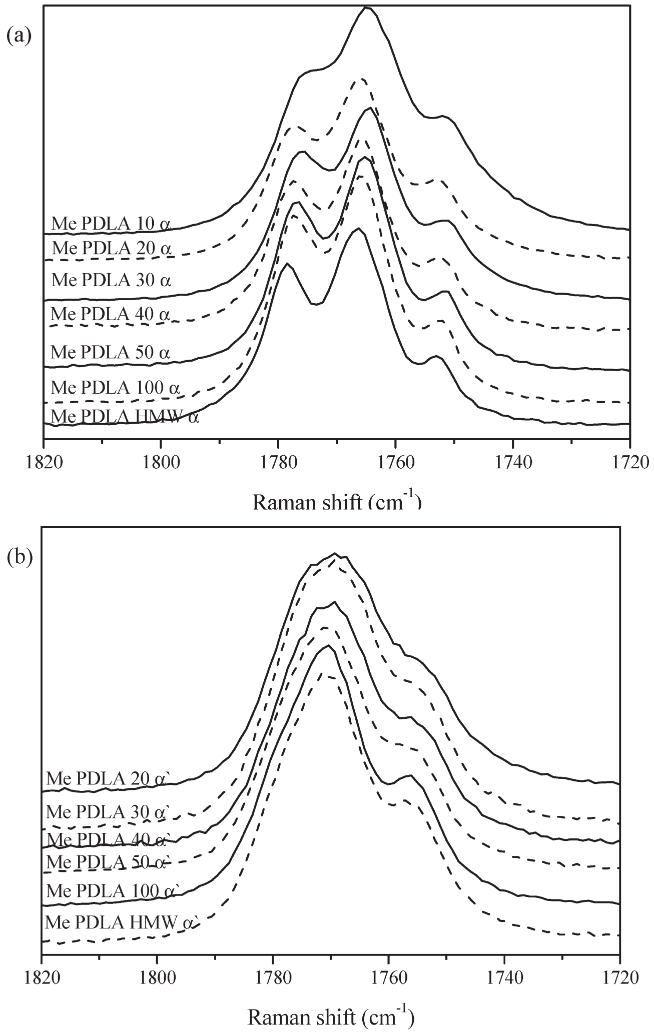

Figure 4. Raman spectra from 1820 to 1720 cm^{-1}; (a) α crystal, (b) α′ crystal.

characterized by the multiplicity of peaks in vibrational spectra of crystalline polymers.[4,26] The α crystalline form is characterized by a splitting in the carbonyl region because of the existence of an ordered arrangement of transition moments along the helical chain[26,34] and a peak at 922 cm^{-1}, which is characteristic of crystallinity in PLA.[4] For α′ crystals the peak at 922 cm^{-1} is observed while the carbonyl region does not exhibit the multiplet structure as seen for the α crystalline state because of the weakened interchain interactions resulting from the less ordered structure. The α′ crystal could not be obtained for the oligomers with DP of 10. Annealing at an undercooling of 90, 80, and 75 °C did not lead to formation of the α′ crystals as indicated by Raman spectra. Annealing at an undercooling of 70 °C leads to the formation of α crystal for this particular oligomer. The Raman spectra for all the methyl-terminated oligomers are shown in Figure 4.

Figure 5 shows the DSC traces of the annealed samples all exhibiting sharp melting endotherms. The absence of a crystallization exotherm in the DSC trace provides further evidence of the samples being completely crystalline. For α crystals the melting temperature and enthalpy of melting increase with increase in molecular weight. On extrapolation of a plot of ΔH

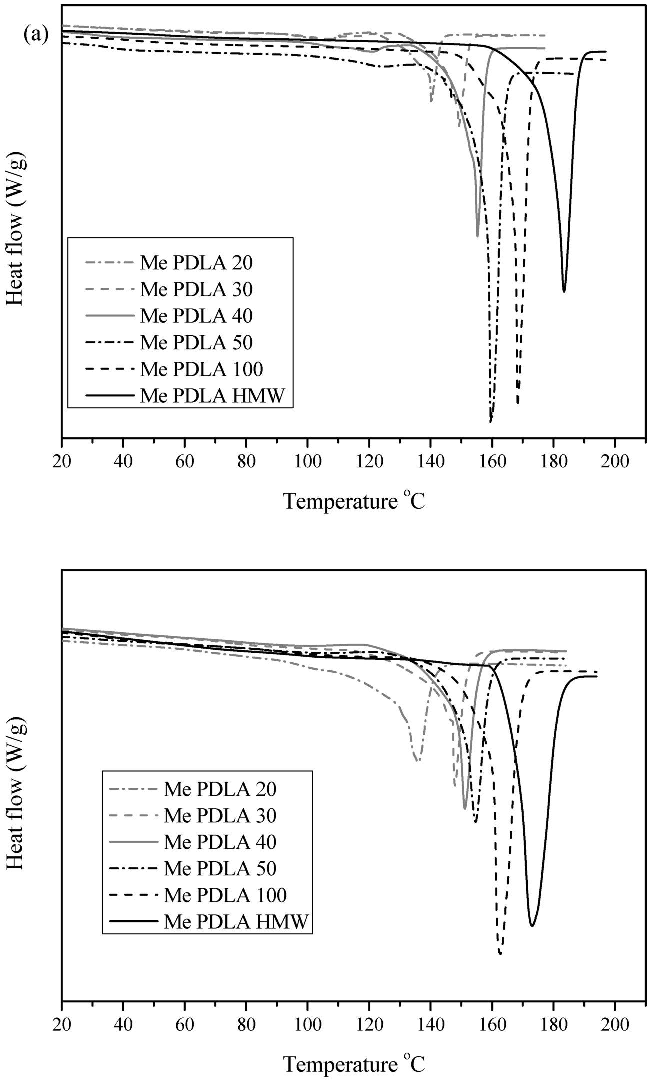

Figure 5. DSC traces of annealed (a) α crystals and (b) α′ crystals (first heating run, 10 °C/min).

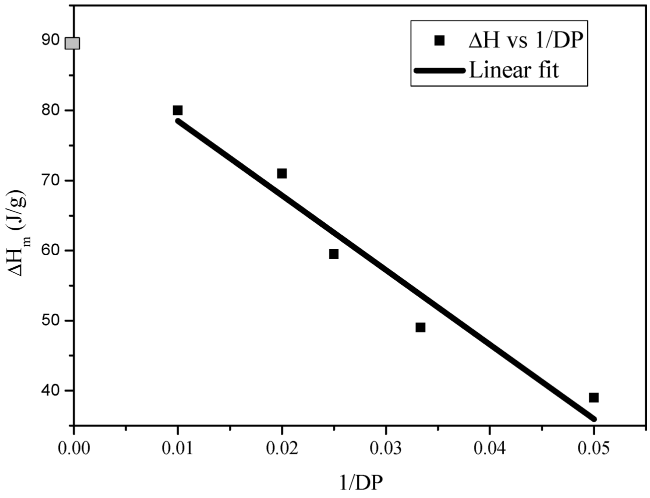

Figure 6. ΔH_m vs 1/DP for α crystals.

Table 2. Thermal Properties of α and α′ Crystals

	α crystal		α′ crystal	
sample	T_m (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)
Me PDLA 20	139	39	136	40
Me PDLA 30	149.5	49	148	45
Me PDLA 40	155	59.5	151	50
Me PDLA 50	159	71	155	60
Me PDLA 100	168.5	79.5	163	60
Me PDLA HMW	183	87.5	173	60

Table 3. End-Group Effect on Melting

sample	T_m (°C)	ΔH (J/g)	sample	T_m (°C)	ΔH (J/g)
Me PDLA 20	140	40	Me PDLA 40	155	60
Et PDLA 20	140	42	Et PDLA 40	154.6	67
nPr PDLA 20	115	39	nPr PDLA 40	151	66
nBu PDLA 20	115	34	nBu PDLA 40	146	59

vs 1/DP to infinite molecular weight, the enthalpy of melting is found to be 89.2 J/g with standard of deviation to be ±4.3 J/g (Figure 6). This is in good agreement with Fisher's original value of 93 J/g. In the case of α′ crystals the enthalpy of melting was found to plateau at a value of 60 J/g, consistent with the value determined in an earlier study.[32] The melting temperatures of α′ crystals were lower than those for α crystals of the same molecular weight (Table 2). The monotonic increase in ΔH_m value for the α crystals suggest that the oligomers form extended chain lamellae. For the α′ crystals ΔH_m plateaus after degree of polymerization of 50. Because of the lower ΔH_m, which implies weaker interchain interactions, it is not surprising that above the DP of 50 (~150 Å in length) the oligomer may exist in chain-folded structure accounting for the departure from linearity. The data obtained for the oligomers provide further evidence of the crystalline packing and thermal stability difference between the α and α′ crystals. Vibrational spectroscopy provides evidence related to the looser crystalline packing in the α′ crystal while thermal data provide evidence related to the observed lower thermal stability of the α′ crystal compared to the α crystal.

Table 3 shows the melting points of annealed samples of oligomers with different end-groups. It can be seen that the effect of end-groups is more pronounced for lower molecular weight oligomers, such as those with DP of 20. The *n*-propyl- and *n*-butyl-terminated oligomers have bulkier end-groups and have melting points 25 °C lower than the methyl- and ethyl-terminated oligomers. For oligomers with DP of 40, the drop in melting point with increase in end-group size is much less pronounced (Table 3). Our data are thus consistent with the Gibbs–Thomson model.

■ CONCLUSIONS

Chain conformation and chain packing in PLA were studied using PDLA oligomers with different molecular weights and end-groups. Experimental data provided evidence for the earlier model proposed which predicted a chain structure dominated by the *tg′t* conformation. The equilibrium melting enthalpy of α crystal of PLA was calculated using the linear relationship between enthalpy of fusion and reciprocal of lamellar thickness for chain-extended crystals, and the value was found (89.2 ± 4.3 J/g) to be in close agreement with one of the reported values (93 J/g). Using a similar analysis, the enthalpy of melting for the α′

phase was determined to be 60 J/g. Using the oligomers, these values were determined using a much more straightforward approach. The effect of end-group on chain conformation was studied, and it was found that the chain conformation is not affected by different end-groups. The effect of end-groups on chain packing was found to be pronounced for oligomers with DP of 20, and the end-group influence decreased with increase in molecular weight.

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