



Enhancing the Sustainability of Poly(Lactic Acid) (PLA) Through Ketene-Based Chain Extension

Yonca Alkan Goksu¹

Accepted: 19 December 2023
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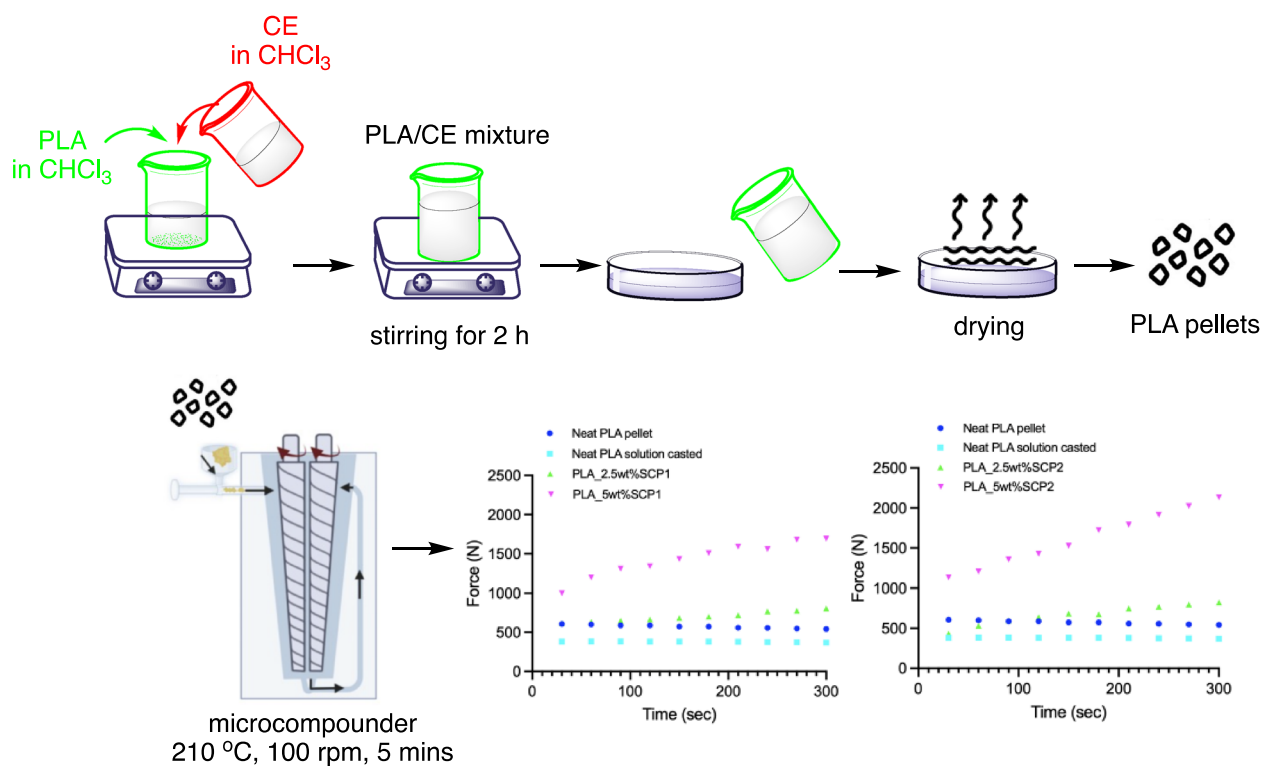
Abstract

The widespread utilization of nonrenewable fossil-based polymers has led to significant environmental damage. Bio-based Poly(lactic acid) (PLA) has garnered substantial academic and industrial interest in the last two decades due to its advantageous characteristics for food packaging applications. Nonetheless, the improper disposal of PLA continues to contribute to the plastic waste problem. PLA recycling mainly involves thermal processes, facing challenges due to PLA's limited stability. This study aims to enhance PLA's molecular weight and melt viscosity by using chain extenders to increase its degree of branching. A modular chain extender capable of thermally forming highly reactive ketene intermediates is employed to react with PLA's hydroxyl and carboxyl end groups in a single step. For this purpose, copolymers of styrene and 2,2,5-trimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione were synthesized using free radical polymerization and characterized through ¹H-NMR, TGA, and DSC analyses. The chemical interaction between these chain extenders and molten PLA was also explored, resulting in increased PLA molecular weight and higher melting temperature (T_m), reaching 155.1 for PLA_2.5CE2. Additionally, the branching introduced through this process led to a notable increase in the UV absorption of PLA, suggesting potential applications in the packaging industry. The chemical tunability of this functional ketene-based chain extender holds promise for tailoring PLA's structure for diverse applications, further advancing its sustainability and utility.

✉ Yonca Alkan Goksu
alkanyo@itu.edu.tr

¹ Department of Metallurgical & Materials Engineering,
Istanbul Technical University, 34469 Maslak, Istanbul,
Türkiye

Graphical Abstract



Keywords PLA · Meldrum's acid · Ketene intermediates · Chain extension

Introduction

The predominant source of plastics that are essential to our society is produced from petroleum-based resources, whereas only a minor fraction is obtained from renewable feedstocks. In 2015, the global production of plastic amounted to 380 million metric tons, wherein the contribution of bio-based materials constituted less than 1% of the overall quantity [1]. The extensive utilization of non-renewable fossil-based polymers has resulted in considerable environmental damage. The use of bio-based polymers constitutes a significant advancement toward tackling these concerns. However, it is crucial to thoroughly evaluate the proper disposal methods for these materials at the end of their lifespan in order to facilitate the transition towards a circular economy for plastic materials [2–4].

Poly(lactic acid) (PLA) is a bio-based polymer that has gained significant academic and industrial attention over the past two decades due to its beneficial properties for food packaging applications [5]. Lactic acid, the primary component, is obtained via fermentation from renewable sources including food crops (such as corn) and waste sugars (such as cellulosic materials [6]). Currently, PLA is

more expensive than petroleum-based counterparts due to high production costs associated with the fermentation and purification of lactic acid, which account for approximately 50% of the total cost [7]. PLA is also produced from the cyclic dimer, lactide (LA), rather than the polycondensation of lactic acid, that could reduce the manufacturing costs [8]. The ring opening polymerization (ROP) of LA has the advantage of not releasing water as a byproduct during propagation which could enable the synthesis of PLA with a significantly elevated molecular weights [9, 10].

Although PLA has the benefit of being a renewably sourced material, its improper disposal still contributes to the plastic waste problem in the environment. Reports about PLA being biodegradable frequently lead to the misconception that this material will rapidly decompose in nature [11]. The decomposition of PLA in soil or domestic composters could take one year at a temperature of 20 °C, while higher temperatures could accelerate the process [12]. Studying the degradation of PLA in marine environments also presents significant challenges due to the multitude of factors and situations that necessitate careful consideration [13, 14].

Since PLA requires time and special environmental conditions to degrade, its mechanical recycling would be

beneficial in the end-of-life phase. The mechanical recycling of PLA involves the collection, cleaning, and reprocessing of the material with the objective of preserving its initial qualities [15]. Reprocessing of PLA is performed thermally and one of the primary challenges connected with this type of recycling is the limited hydrolytic and thermal stability of PLA. Hence, PLA is prone to chain scission, decrease in its average molecular weight and subsequent decline of its mechanical properties is mostly observed [16–18].

Leveraging chain extenders allows the modulation of melt viscosity and thermal stability, thereby preventing degradation. Chain extension, a type of post-polymerization modification, includes chemical reactions to increase molecular weight of condensation polymers. This is achieved by inducing chain branching with the use of multifunctional chemicals during the melt compounding process [19]. Chain extenders include two or more reactive chemical functionalities such as anhydrides [20–23], isocyanides [24], and epoxides [25–27]. These functional groups have the ability to undergo reactions with the reactive end groups of polymers. Among these, Joncryl ADR, also known as multifunctional styrene–acrylate–glycidyl methacrylate copolymer, is one of the most commonly used chain extenders to enhance the melt strength of matrix polymer or to act as a compatibilizer to increase the adhesion between filler and the dominant phase by reacting with the hydroxyl and/or carboxyl terminal groups of polyesters through its functional epoxide groups [28–33].

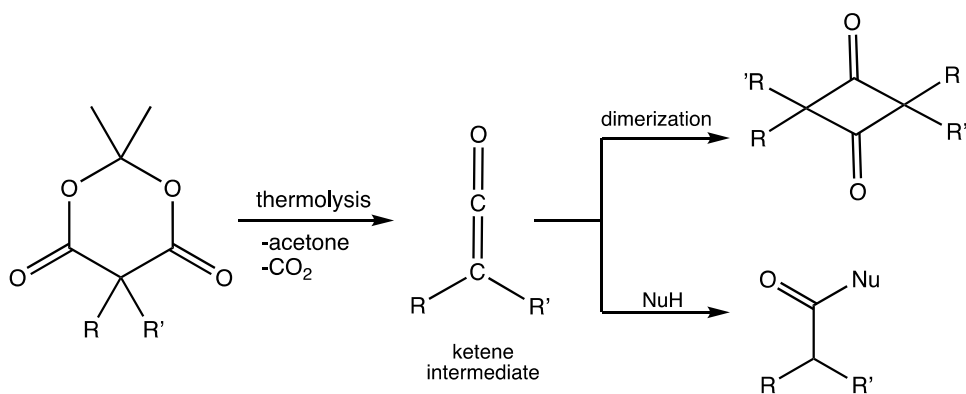
Studies on PLA/Joncryl systems revealed an improvement in elongational and shear rheological properties, as well as an increase in molecular weight and its distribution due to chain extension processes [34, 35]. In their study, Mihai et al. [36] produced branched polylactic acid (PLA) through the addition of Joncryl, resulting in enhanced shear viscosity and melt elasticity. The findings presented by Corre et al. [37] have also shown that the introduction of Joncryl resulted in the addition of a high molecular weight shoulder to the monomodal molecular weight distribution (MWD) of pure polylactic acid (PLA) due to chain extension.

In another study conducted by Al-Itry et al. [38], it was revealed that the introduction of Joncryl into PLA/PBAT through reactive extrusion resulted in an improvement of their thermal stability. The study conducted by Kahraman et al. [39, 40] also demonstrated that the addition of Joncryl in PLA and TPU blends resulted in an enhanced level of interfacial compatibility.

Due to the fact that the chain extension reaction takes place between Joncryl and the hydroxyl or carboxyl reactive-end groups of PLAs, the reactivity of these groups is of critical importance. In their study, Cailloux et al. [41] demonstrated that the selectivity of the interaction between epoxy groups and carboxyl end groups of PLA chains exhibited a greater degree of selectivity when compared to the reaction between epoxy and hydroxyl groups. Owing to the limited presence of carboxylic groups on the polymer chains of commercial PLAs, their ability to engage in branching reactions, similar to polyethylene terephthalate (PET) is hindered [42]. Consequently, certain researchers have employed a two-step reaction approach to address this issue. Liu et al. [43] employed pyromellitic dianhydride (PMDA), which is characterized by an anhydride functional group, and triglycidyl isocyanurate (TGIC), which possesses an epoxide functional group, in order to attain the desired branched structures. Additionally, Gu et al. [44] utilized a tri-functional aziridine linker, trimethylolpropane tris(2-methyl-1-aziridinepropionate) (TTMAP), for chain extension of PLA via a two-step reaction with PMDA.

The main goal of this research to increase the molecular weight, and hence melt strength, of PLA by using a chain extender that has a high reactivity to both hydroxyl and carboxyl end groups via one-step process. Therefore, use of highly reactive ketene intermediates could be a promising strategy [45]. These intermediates could be formed in situ through thermolysis of Meldrum's acids (Fig. 1) and in the absence of nucleophiles, they could give [2 + 2] cycloaddition reaction to form cyclobutane-1,3-dione ring. However, in the presence of nucleophiles, ketenes readily react with them to form the corresponding ester or amines

Fig. 1 Thermolysis of 5,5-dialkyl Meldrum's acid to a ketene, and its reactivity towards nucleophiles



[46, 47]. Since PLA has both the carboxylic and hydroxyl terminal groups as nucleophiles, in situ formed ketenes could react them easily without dimerization. The selection to focus on ketenes as a target functional group has been driven by its extensive background in the field of organic chemistry and its customizable reactivity towards majority of nucleophiles. Despite being discovered by Staudinger in 1905 [48] and extensively utilized in sophisticated small-molecule syntheses, the full potential of ketenes as a versatile functional group in polymer and materials science remains largely unexplored even after more than a century [49]. The pioneering studies on the utilization of ketenes on polymer science by Hawker and Leibfarth showed that thermally generated ketenes derived from Meldrum's acid derivatives have proven to be valuable precursors for a diverse array of macromolecular architectures [46, 50–53].

This article reports a modular approach to use ketene intermediates as a reactive chain extender to increase the molecular weight and branching of PLA. To the best of our knowledge, there is no example of utilization of ketenes for chain extension processes. For this purpose, copolymers of styrene and 2,2,5-trimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione were synthesized through free radical polymerization and their reactivity towards PLA in molten state was investigated.

Experimental

Materials

2,2,5-trimethyl-1,3-dioxane-4,6-dione was purchased from Sigma Aldrich and were used as received. Styrene (St, 99% Aldrich) and 1-chloromethyl-4-vinyl benzene (90%, Aldrich) were passed through basic alumina column to remove the inhibitor. K_2CO_3 (Merck), $NaHCO_3$ (Merck), $MgSO_4$ (Aldrich), Azobisisobutyronitrile (AIBN, 98%, Fluka), acetone (Merck), hydrochloric acid (HCl, 1 N, Merck), ethyl acetate (EtOAc, Merck) and hexane (Hex, Merck) were used as received. Dry N,N-dimethylformamide (DMF) was obtained from solvent still. PLA Ingeo 4043D was purchased from NatureWorks with MFR value of 6 g / 10 min.

Synthesis of 2,2,5-trimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione [1]

2,2,5-trimethyl-1,3-dioxane-4,6-dione (2.0 g, 13 mmol), and K_2CO_3 (2.0 g, 14.5 mmol) were placed in 40 mL of acetone and stirred for 30 min. 1-chloromethyl-4-vinyl benzene (2.0 mL, 14.0 mmol) was added dropwise at room temperature and the reaction mixture was heated to 55 °C and refluxed for 48 h. After evaporation of acetone in vacuo, remaining solid was quenched by 1 N HCl and

extracted with EtOAc. Organic phase was washed with water (2 × 50 mL) and saturated aqueous $NaHCO_3$ solution (2 × 50 mL). Combined organic extracts were dried over $MgSO_4$, filtered and concentrated to give a yellowish solid. The final product was purified by column chromatography (EtOAc/Hex : 1/5, R_f = around 0.3) (1.5 g, 42% yield). 1H -NMR (600 MHz, $CDCl_3$): δ 7.32 (d, J = 7.2 Hz, 2 H), 7.15 (d, J = 7.2 Hz, 2 H), 6.67 (dd, J = 17.6 and 10.9 Hz, 1 H), 5.73 (d, J = 17.6 Hz, 1 H), 5.24 (d, J = 10.9 Hz, 1 H), 3.33 (s, 2 H), 1.76 (s, 3 H), 1.61 (s, 3 H), 0.98 (s, 3 H). ^{13}C -NMR (150 MHz, $CDCl_3$): δ 169.73, 136.98, 136.20, 134.78, 130.21, 126.43, 114.04, 105.19, 52.09, 44.62, 29.36, 28.35, 25.71.

Synthesis of Poly(S-r-[1]) (CE) Copolymers

Two different chain extender copolymers were synthesized with a different ratio of styrene and [1] monomers. General procedure for CE containing 50% of [1] is given as follows:

Styrene (0.46 g, 4.4 mmol), [1] (1.19 g, 4.35 mmol) and 2,2'-azobis(2-methylpropionitrile) (AIBN) (71 mg, 0.43 mmol) was dissolved in 10 mL of dry DMF in a Schlenk tube and the mixture was subjected to three freeze-pump-thaw cycles. Then, Schlenk tube was placed in an oil bath that was previously adjusted to 80 °C and stirred for 4 h. The resulting polymer was precipitated in cold methanol. The monomer feed composition for CE1 and CE2 is given in Table 1.

Preparation of PLA/CE Samples

PLA and CEs were separately dissolved in 10 mL of chloroform and after complete dissolution they were combined and stirred for extra 2 h at room temperature (Table 2). PLA/CE mixture was then poured into petri glass dish and left to dry under fume hood for 24 h and they were further dried in vacuum oven at 60 °C for 24 extra hours.

After samples were fully dried, obtained PLA films were cut into small pieces and they were separately processed in micro compounder (Xplore Instruments Micro compounder 5 mL: MC 5) at 210 °C, 100 rpm for 5 min.

Table 1 Monomer feed composition of CE1 and CE2

	Styrene	[1]
CE1 ^a	0.46 g (4.4 mmol)	1.19 g (4.4 mmol)
CE2 ^a	0.63 g (6.09 mmol)	0.70 g (2.6 mmol)

^aPolymerization reactions were conducted in the presence of AIBN (0.43 mmol) and dry DMF (10 ml) at 80 °C for 4 h

Table 2 Preparation of PLA/CE Samples

	PLA 4043D (mg)	CE Type	CE (mg)	CE (%)	Conditions
Neat PLA ^a	2000	–	0	0	210 °C,
Neat PLA_SC ^b	2000	–	0	0	100 rpm,
PLA_2.5CE1	1950	CE1	50	2.50	5 min,
PLA_5.0CE1	1900	CE1	100	5.00	Under N ₂
PLA_2.5CE2	1950	CE2	50	2.50	
PLA_5.0CE2	1900	CE2	100	5.00	

^aPLA directly used^bPLA was solution casted without any CE

¹H-Nuclear Magnetic Resonance (¹H-NMR) Analysis

¹H-NMR of the synthesized [1] monomer, CE1 and CE2 samples were recorded at room temperature on a Bruker AVANCE III 600 MHz using CDCl₃ as the solvent.

Gel Permeation Chromatography (GPC) Analysis

GPC analysis of CE1 and CE2 samples were conducted using a Tosoh EcoSEC Elite GPC system, equipped with a TSKgel Super HM-M (17392) column. The column was kept at a temperature of 40 °C and was coupled with a refractive index (RI) detector and a Tosoh LENSTM 3 multi-angle light scattering detector (MALS). The mobile phase utilized in this experiment was tetrahydrofuran, at a flow rate of 0.5 mL/min. The molecular weight and dispersity values are presented with respect to polystyrene standards.

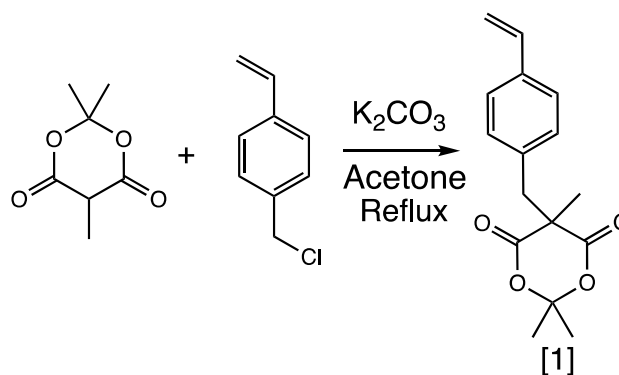
Termogravimetric Analysis (TGA)

[1], CE1 and CE2 samples were analyzed using a TGA (TA instruments with Q50 apparatus). Experiments were carried out under nitrogen at a heating rate of 10 °C/min up to 600 °C.

Differential Scanning Calorimetry (DSC) Analysis

The DSC analysis was conducted in a TA Instruments equipment, model QS100, using nitrogen as purge gas in a continuous flow of 50 mL min⁻¹. Samples were initially heated from 0 to 250 °C at a heating rate of 10 °C/min. The degree of crystallinity (X_c) of PLA samples were determined using Eq. (1):

$$X_c^{heating} = \frac{\Delta H_m - \Delta H_{cc}}{w_{PLA} \times \Delta H_m^0} \times 100 \quad (1)$$

**Fig. 2** Synthesis of 2,2,5-trimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione [1]

Here W_{PLA} is the PLA weight fraction, ΔH_m and ΔH_c are the heat enthalpies of melting and crystallization, respectively. ΔH_m^0 is the heat of fusion required to melt 100% crystalline PLA, which is given as 93.6 J/g [54].

UV Analysis

UV spectra of PLA/CE samples were recorded on a Shimadzu UV-1601 spectrometer. The resolution was 4 cm⁻¹ and 24 scans were averaged with a 0.2 cm s⁻¹ scan speed. PLA/CE samples were also dissolved in DCM and their concentration was kept at 10 mg/mL.

FTIR Analysis

FTIR spectra of the samples were recorded at room temperature in the mid-IR range (400–4000 cm⁻¹) using a Bruker FTIR spectrometer equipped with a Bruker Platinum ATR accessory. Sample measurements were conducted on dried powders. Each spectrum was taken over 12 scans with a resolution of 2 cm⁻¹. The obtained results were analyzed using OPUS software (Bruker Optics).

Results and Discussion

In order to synthesize polymers containing Meldrum's acid moieties, firstly, 2,2,5-trimethyl-1,3-dioxane-4,6-dione was reacted with p-chloromethyl styrene and [1] was obtained in a moderate yield and characterized by spectral analysis (Fig. 2). ¹H-NMR spectrum of [1] presented in Fig. 3a clearly displays the characteristic peaks emerging from -CH₃ protons of Meldrum's acid at 1.76, 1.61 and 0.98 ppm. Vinylic protons of styrene is also clearly visible at 6.67 and 5.73 ppm. ¹³C-NMR spectrum of [1] also supports the chemical structure (Fig. 3b).

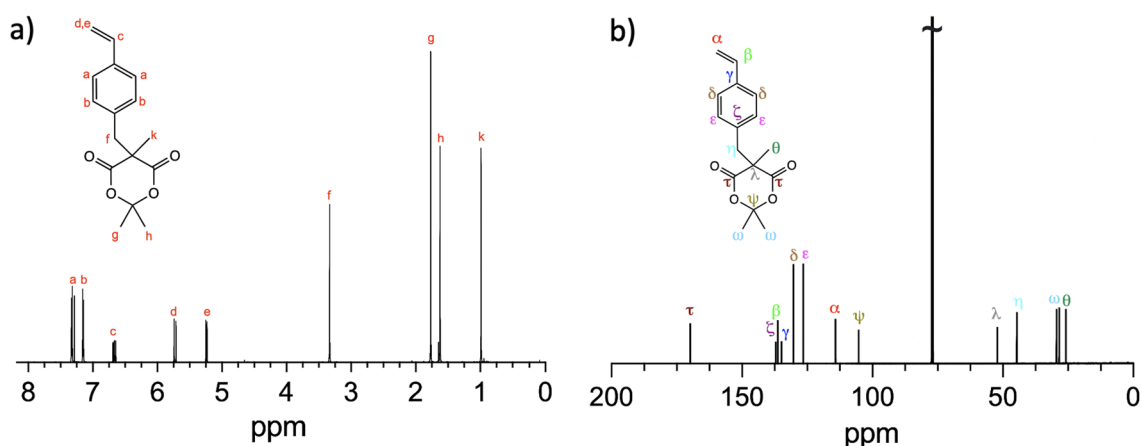


Fig. 3 a ^1H -NMR and b ^{13}C -NMR spectrum of 2,2,5-trimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione [1]

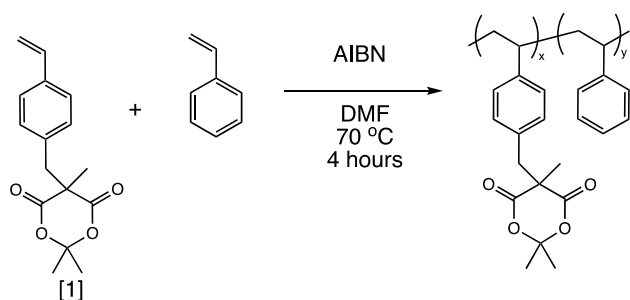


Fig. 4 Copolymerization of styrene and [1]

Free radical copolymerization of styrene and [1] monomers at different ratios in the feed mixture was carried out by using conventional AIBN initiator (Fig. 4). Obtained copolymers were identified with CE1 and CE2 notations and their compositions and molecular weights were summarized in Table 3. Also, GPC traces of CE1 and CE2 are shown in Fig. 5.

The ^1H -NMR spectra of CE1 and CE2 are depicted in Fig. 6a and b. Based on the findings presented, it can be shown that a reduction in the quantity of [1] monomer in the monomer feed leads to a drop in the signal intensities of $-\text{CH}_2$ and $-\text{CH}_3$ from Meldrum's acid at 3.33 (denoted as "a" in the structure) and 0.98 ppm, respectively, within the polymer backbone. In order to further quantify this, the ratio of signal intensity ratio of "a" proton to total aromatic protons were calculated as 0.23 and 0.17 for CE1 and CE2, respectively. The observed decrease in this ratio confirms the lower amount of Meldrum's acid bearing unit in CE2 structure.

FTIR spectra of CE1 and CE2 also confirms their chemical structure (Fig. 7). $\text{C}=\text{O}$ stretching bands of Meldrum's acid unit is available at 1734 cm^{-1} as well as aromatic $\text{C}-\text{H}$ bending bands at 696 cm^{-1} .

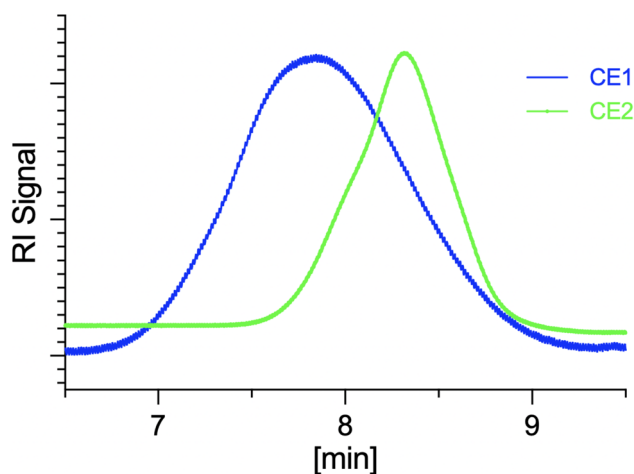


Fig. 5 GPC traces of CE1 and CE2

Figure 8a presents an illustration of the differential scanning calorimetry (DSC) spectra of CE1 and CE2. At approximately $200\text{ }^\circ\text{C}$, the endothermic process of ketene formation commences. An analysis of the normalized heat flow versus temperature graphs obtained through DSC analysis reveals that the area beneath the endotherm, which begins at approximately $200\text{ }^\circ\text{C}$, is significantly diminished in the case of CE2. The observed results suggests that CE1 has a higher enthalpy for ketene formation due to an increased abundance of Meldrum's acid bearing units within its structure. These findings are also supported via thermogravimetric analysis (TGA) (Fig. 8b). When both monomer ratios and mass loss due to CO_2 and acetone release during the ketene formation from Meldrum's acid taken into account, the weight% of [1] monomer in CE1 and CE2 was calculated from TGA (Fig. 8b) as 45 and 31%, respectively which is in a good alignment with the monomer ratios in the feed.

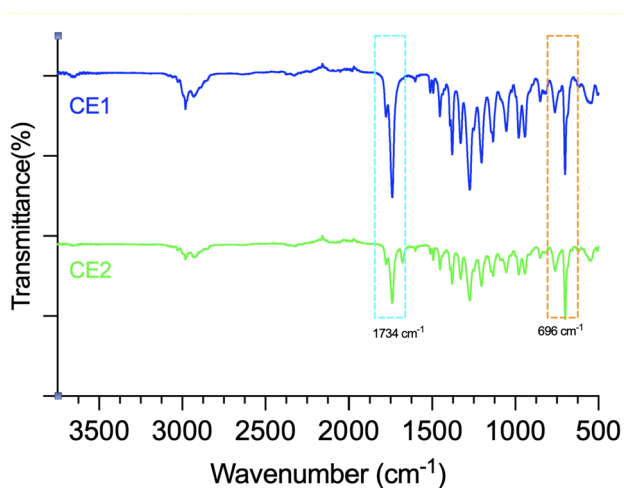
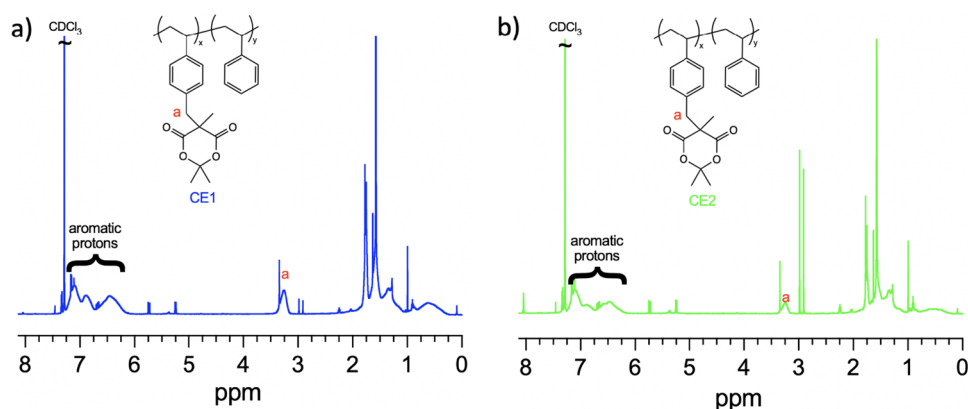
Table 3 Copolymerization^a of [1] and Styrene

	Monomer in feed (mol%)		Conversion ^b (%)	M _n ^c (g mol ⁻¹)	M _w ^c (g mol ⁻¹)	M _w /M _n ^c
	[1]	Styrene				
CE1	50	50	28.4	8879	14,797	1.67
CE2	30	70	33.3	4816	7935	1.65

^aPolymerizations were conducted at 70 °C for 6h in the presence of AIBN (0.04 M)

^bOverall conversion determined gravimetrically

^cDetermined by GPC measurements according to polystyrene standards

Fig. 6 ¹H-NMR spectra of CE1 and CE2**Fig. 7** FTIR spectra of CE1 and CE2

After characterization of synthesized CEs, they were mixed with PLA by solution casting. Firstly, PLAs and CEs separately dissolved in CHCl_3 . Those mixtures were combined and stirred for extra 2 h, then they were poured into a petri dish to dry. PLA films were obtained by evaporating the solvent after mixing synthesized CEs and PLA in CHCl_3 at ratios of 2.5 and 5wt% (Fig. 9). The films were cut into pieces and were subsequently mixed within a micro compounder operating at a temperature of 210 °C and a rotational speed of 100 rpm for a duration of

5 min. The force versus time graphs obtained during this compounding process depicted in Fig. 10. The dynamic interplay of mechanical forces within an extruder can offer crucial insights into the evolving mechanical properties of the polymer material. When the force values exhibit a noticeable increase over the course of the extrusion process, it is commonly associated with a significant enhancement in mechanical strength and resistance, as the polymer undergoes a sequence of structural alterations. The increasing strength of the material serves as evidence of its capacity to endure and adjust to the mechanical strains and shear pressures that are inherent in the extrusion process. Obtained GPC results for neat PLA, Neat PLA_SC and chain extended PLAs are illustrated in Fig. 11 and summarized in Table 4 that are compatible with the force-versus-time profiles recorded during the compounding process. Molecular weight of PLA decreased after solution casting process (neat PLA_SC), but that decrease was compensated by the addition of CEs.

Upon addition of the CEs into the PLA matrix, decrease in the polydispersity index (M_w/M_n) of PLA was observed which necessitates further explanation. There are several studies in the literature that analyzes the molecular weight and molecular weight distribution of PLA upon addition of commercial chain extender, whose trade name is Joncryl. As stated earlier, Joncryl is multifunctional styrene–acrylate–glycidyl methacrylate copolymer, bearing epoxide units that could react with

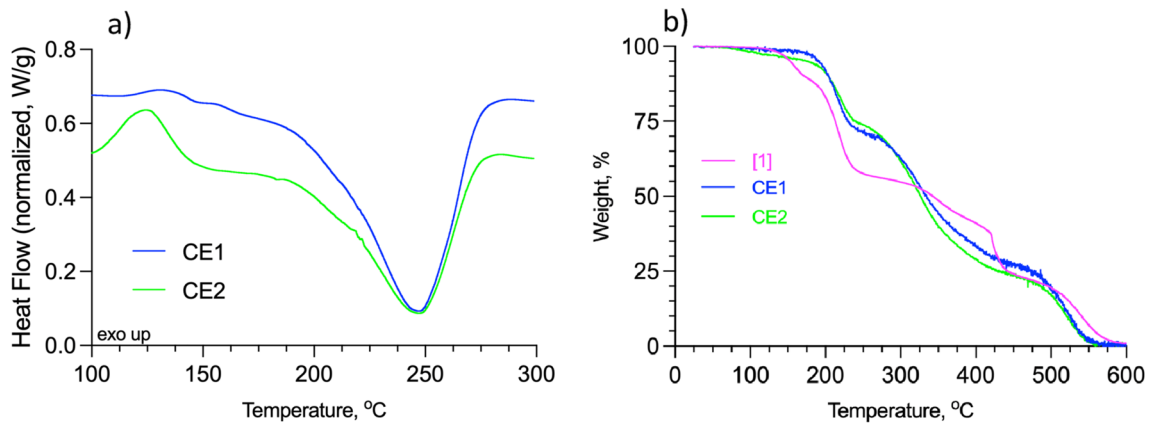


Fig. 8 a DSC spectra CE1 and CE2 and b TGA (right) spectra of [1], CE1 and CE2

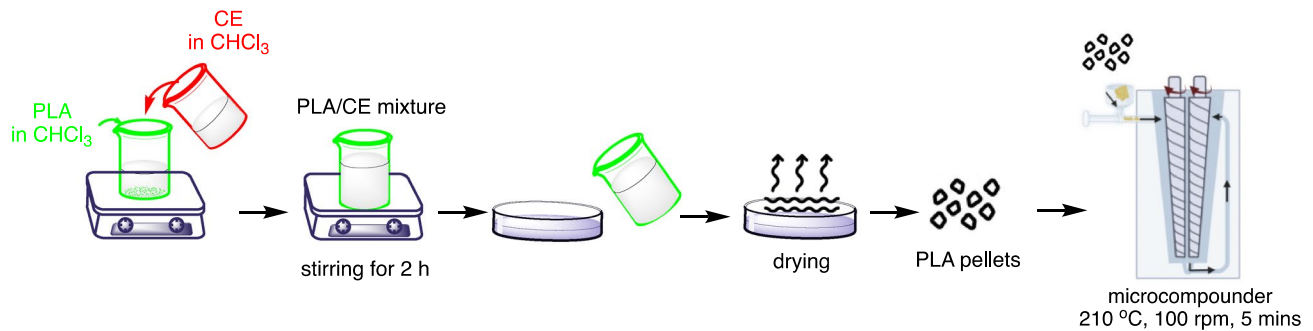


Fig. 9 Schematic representation of solution casting process

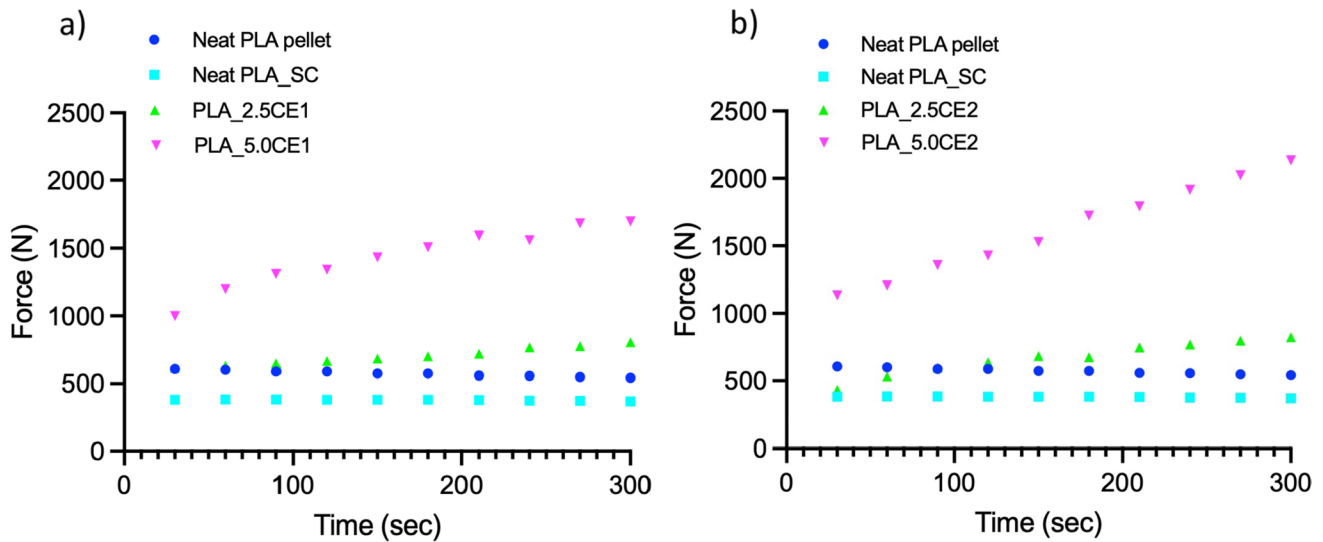


Fig. 10 Time vs. force graphs of a PLA_2.5CE1, PLA_5.0CE1 and b PLA_2.5CE2, PLA_5.0CE2

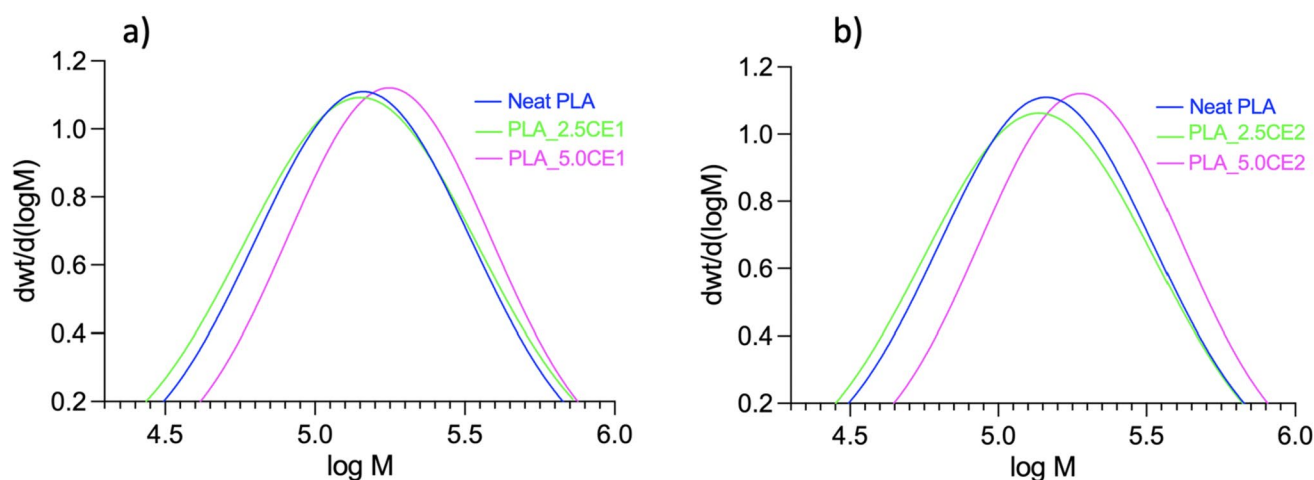


Fig. 11 GPC traces of **a** PLA_2.5CE1, PLA_5.0CE1 and **b** PLA_2.5CE2, PLA_5.0CE2

Table 4 GPC measurements of neat PLA, Neat PLA_SC and chain extended PLA samples

Sample	M_n^a (kg mol^{-1})	M_w^a (kg mol^{-1})	M_w/M_n^a
Neat PLA	90.5	140.4	1.55
Neat PLA_SC	76.8	130.2	1.69
PLA_2.5CE1	96.6	153.4	1.59
PLA_5.0CE1	120.2	168.3	1.40
PLA_2.5CE2	94.8	152.7	1.61
PLA_5.0CE1	130.4	170.2	1.30

^aDetermined by GPC measurements according to polystyrene standards and CHCl_3 as the solvent

the chain ends of PLA. There are several types of Joncryl with different epoxide functionalities. Najafi et al. [55] used PLA 4032D which is a semi-crystalline material comprising 2% of D-LA. Upon 1 wt% addition of Joncryl, MW of the PLA increased from 101 kg/mol to 180 kg/mol with an increase in PDI value from 1.86 to 2.85. On the other hand, Grigora et al. [56] used PLA 3052D with much lower molecular weight than that of what Najafi et al. used, a slight decrease in PDI was observed upon addition of CE. According to the GPC results of another study conducted by Jaszkiwicz et al. [57], in which PLA 3051D with 3.7–4.6 D-LA content was used, PDI value was increased addition of CE up to 3 wt%, however a decrease was observed with 5 and 10 wt% addition. Those three examples all used different type of Joncryl as a chain extender as well as different PLAs. It could be concluded that both type of PLA and functionality of Joncryl affected the final molecular weight and molecular weight distribution. In this study, PLA 4043D with 4.5–5 wt% of D-LA content was used and chemical reactivity of proposed ketene-based chain extender might be different

than that of epoxides in Joncryl and it might be possible to conduct other studies to better investigate how the molecular weight and D-content of PLA effects the final chain extension reactions.

The $^1\text{H-NMR}$ spectrum of neat PLA and PLAs compounded with CE1 and CE2 are illustrated in Fig. 12a and b, respectively. The resonance peaks observed at 5.19 and 1.61 ppm in both spectra can be attributed to the presence of methine ($-\text{CH}$) and methyl ($-\text{CH}_3$) protons of the middle repeat units of PLA that are located at locations a and b. The ratio of the integrated peak intensities is equal to 1:2.91, 1:2.95, 1:2.87, 1:2.94, 1:2.92 for neat PLA, PLA_2.5CE1, PLA_5.0CE2, PLA_2.5CE1 and PLA_5.0CE2, respectively that are in a good alignment with the theoretical value of 1:3. The resonance signals at 4.38 ppm is assigned to the methine protons at the a' positions. When a/a' ratios are investigated, 1000:3.4 was observed for neat PLA which is somehow in a good alignment with the obtained results by Meng *et al.* [22]. a/a' ratios for PLA_2.5CE1, PLA_5.0CE2, PLA_2.5CE1 and PLA_5.0CE2 are 1000:3.2, 1000:2.8, 1000:3.2 and 1000:2.7, respectively. Although the analysis of the integration ratios may aid in revealing the molecular structure of the investigated polymeric materials to some extent, simultaneously occurring chain extension and thermal degradation reactions may cause some challenges in properly understanding the molecular structure.

The FTIR spectra of PLA, PLA_2.5CE1, PLA_5.0CE1, PLA_2.5CE2, and PLA_5.0CE2 are depicted in Fig. 13. While the $-\text{C}=\text{O}$ stretching bands of the Meldrum's acid unit are clearly observable at 1734 cm^{-1} in Fig. 6, they cannot be identified when CEs are compounded with PLA due to the robust $-\text{C}=\text{O}$ stretching vibration inherent in their own structure. Additionally, the aromatic protons related to the CEs are also indiscernible in the FTIR spectrum due to significant overlaps.

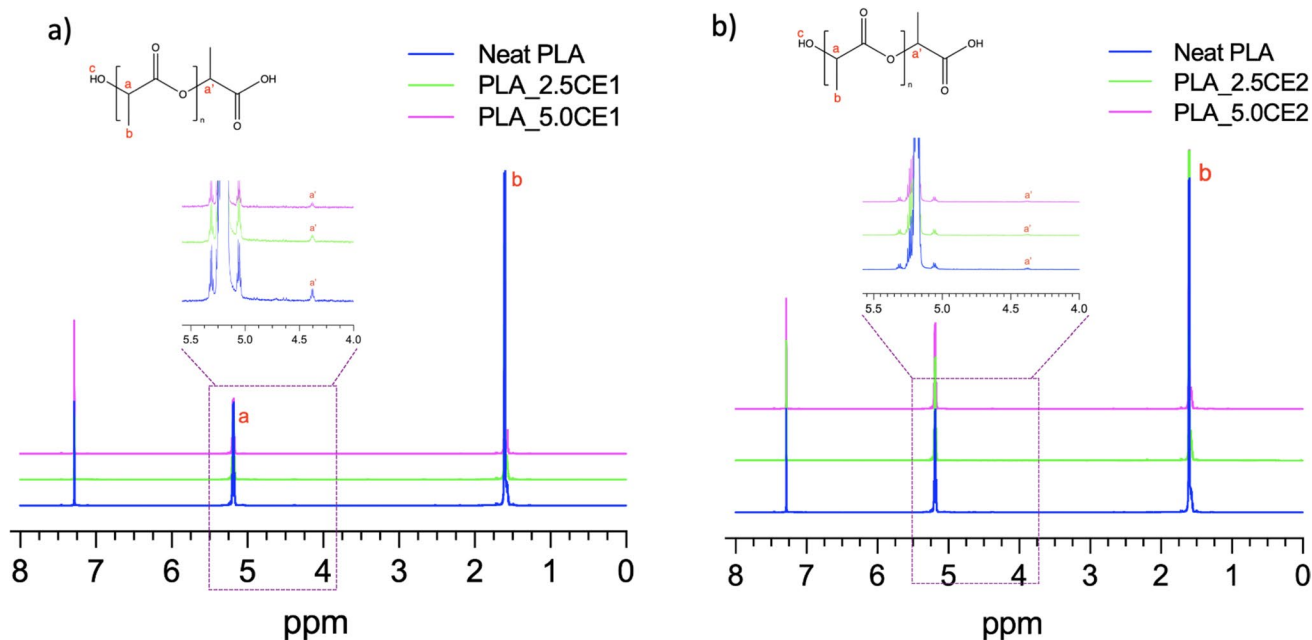


Fig. 12 ^1H -NMR spectra of **a** neat PLA, PLA_2.5CE1 and PLA_5.0 CE1 and **b** neat PLA, PLA_2.5CE2 and PLA_5.0 CE2

DSC thermograms of neat PLA, processed PLA after solution casting and PLA/CE samples are shown in Fig. 14 and obtained data is summarized in Table 5. In addition to Meldrum's acid segments in the CE structure, styrene segments were introduced to promote crystallization [58]. However, upon addition of CE into the matrix, the crystallinity of PLA reduced significantly as a result of the formation of a long chain branching structure [34]. When the PLA_2.5CE1 and PLA_2.5CE2 samples are compared, the melting temperature (T_m) increased to 153.9 and 155.1, respectively. While the percent crystallinity of PLA_2.5CE1

is down to 0.06, due to higher styrene content PLA_2.5CE2 has a percent crystallinity of 1.46. Along with this data, the crystallization temperature is shifted from 113 (for neat PLA) to 121.2 and 122.5 °C for PLA_2.5CE1 and PLA_2.5CE2, respectively. The reduction in chain mobility resulting from the increase in molecular weight and the presence of long chain branches is accountable for the decrease in glass transition temperature (T_g), crystallinity and the increase of the cold-crystallization temperature. In the case of 5 wt% addition of CE1 and CE2, the change in T_g and T_m is not significant and obtained percent crystallization values do not follow a trend. 5 wt% addition of CE might have resulted in highly branched structures that prevented further reaction.

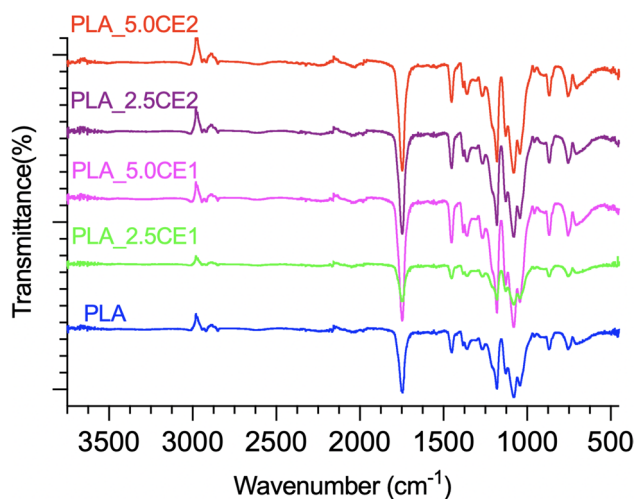
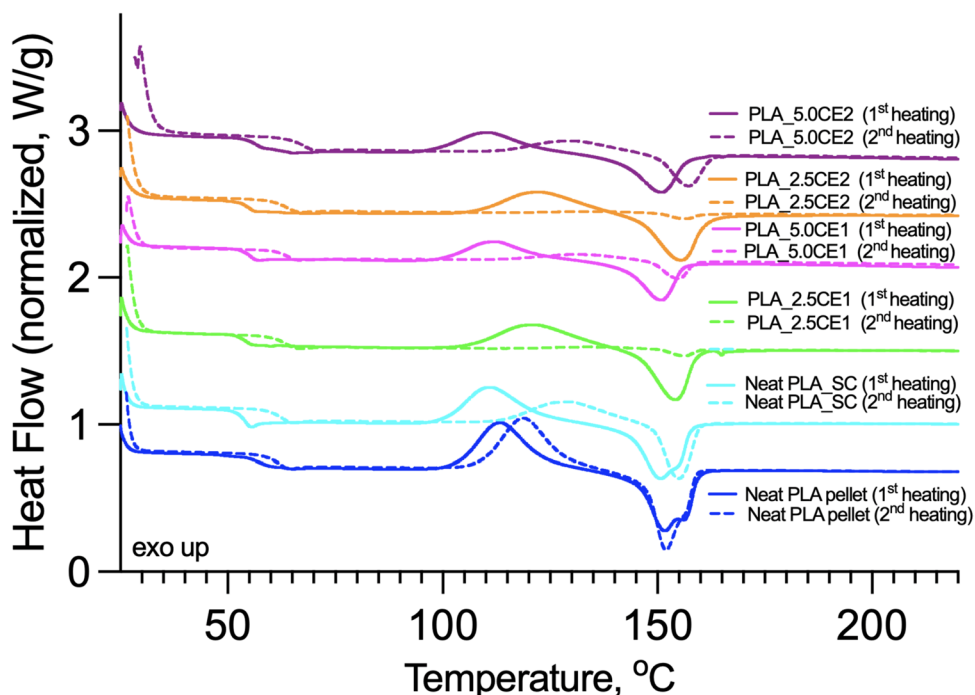


Fig. 13 FTIR spectra of PLA, PLA_2.5CE1, PLA_5.0CE1, PLA_2.5CE2, and PLA_5.0CE2

UV spectra of neat PLAs and chain-extended PLAs are shown in Fig. 15. As the amount of chain extender increased, the corresponding UV absorption also increased. Network PLA tends to have improved UV absorbance as compared to its linear counterpart as a result of reduced chain mobility. To better absorb and dissipate UV radiation might prevent some of that energy from reaching underlying layers or materials. This absorption could be useful in packaging applications, as it could help to protect sensitive components or substrates from UV damage. One potential drawback of network PLA is that it may become less transparent or even opaque as a result of chain extension reaction. While this opacity could be an advantage in applications where UV protection is essential (e.g., outdoor use), it may not be suitable for applications that require transparency like packaging. However, the composition of the chain extender

Fig. 14 DSC thermograms of neat PLA pellet, neat PLA_SC, PLA_2.5CE1, PLA_5.0CE1, PLA_2.5CE2 and PLA_5.0CE2



and the degree of branching could be tailored via this modular approach.

Conclusions

In conclusion, this study has introduced a versatile and modular approach that leverages ketene intermediates as reactive chain extenders to augment the molecular weight of poly(lactic acid) (PLA) while introducing branching. Initially, copolymers bearing Meldrum's acid groups were synthesized through free radical polymerization with varying compositions and meticulously characterized through structural and thermal analyses. Subsequently, these copolymers were blended with PLA through solution casting, ensuring thorough mixing, and then processed in a compounder. The force-versus-time profiles recorded during

the compounding process demonstrated a significant increase in force values, indicative of structural modifications within the PLA matrix. This enhancement in mechanical strength and resistance underscores the potential for improving PLA's performance characteristics. Obtained GPC results also supported those findings as the molecular weight of PLA increased upon addition of chain extenders. Additionally, the introduction of branching led to an observable rise in the UV absorption of PLA, suggesting practical applications in the packaging industry. The inherent chemical adaptability of this innovative chain extender promises a tailorable PLA structure to suit specific requirements. This highly efficient, modular, and reproducible ketene-based methodology for chain extension reactions opens up promising avenues for application across various polyester and polyamine materials. It should also be noted that the release of CO₂ and acetone at temperatures surpassing 200 °C by Meldrum's acid derivatives could offer novel opportunities for research in foaming applications. Ongoing investigations in this research direction are poised to further expand our understanding and applications in this domain.

Table 5 DSC analysis of neat PLA pellet, neat PLA_SC, PLA_2.5CE1, PLA_5.0CE1, PLA_2.5CE2 and PLA_5.0CE2

	T _g (°C)	T _m (°C)	% χ ^c
Neat PLA pellet	56.9	151.4	1.61
Neat PLA_SC	53.9	150.4	1.94
PLA_2.5CE1	54.3	153.9	0.06
PLA_2.5CE2	54.0	155.1	1.46
PLA_5.0CE1	55.4	150.7	1.74
PLA_5.0CE2	56.5	150.6	0.64

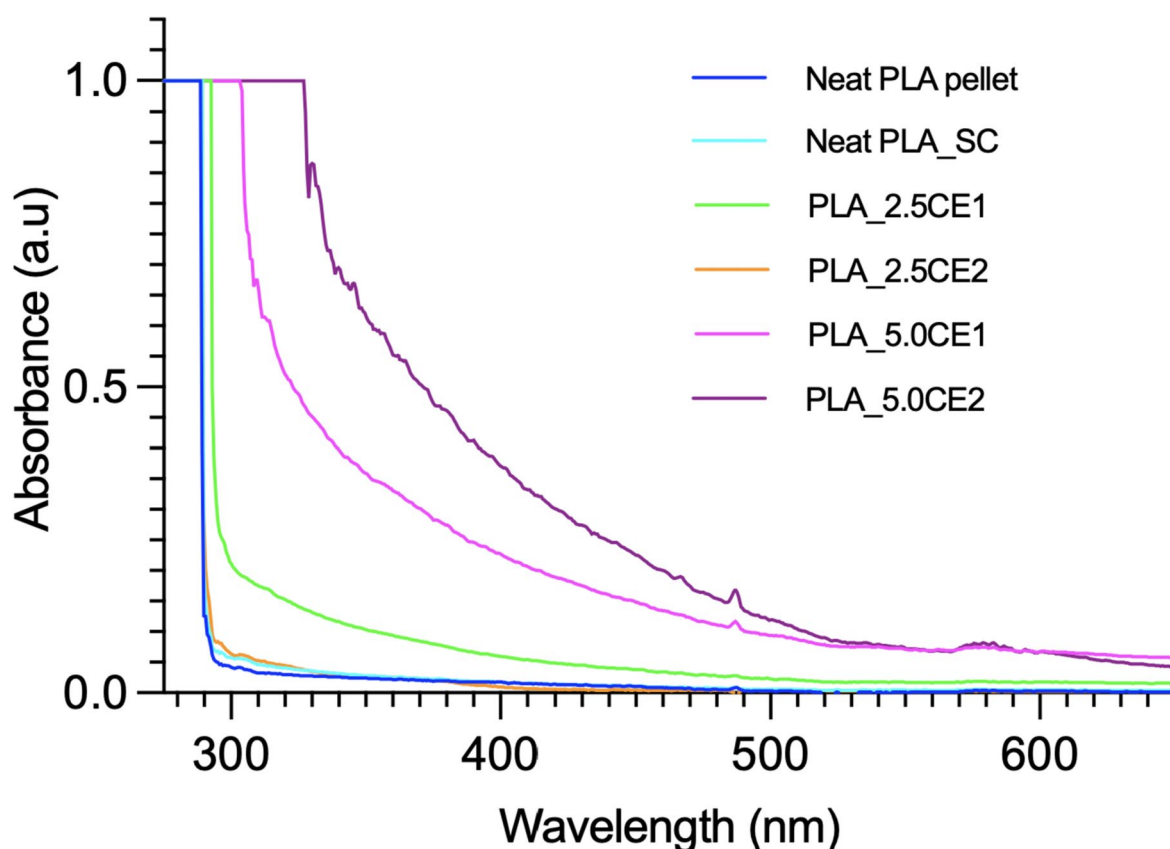


Fig. 15 UV spectra of neat PLA pellet, neat PLA_SC, PLA_2.5CE1, PLA_5.0CE1, PLA_2.5CE2 and PLA_5.0CE2

Acknowledgements This paper is dedicated to the memory and enduring legacy of my PhD advisor, Prof. Yusuf Yagci, whose guidance and contributions to the field of polymer chemistry remain a constant source of inspiration. Additionally, I would like to extend my gratitude to Frank Leibfarth and Leibfarth Research Group for the invaluable opportunities they have provided, as well as to Fulbright and TÜBİTAK 2219 for their substantial financial assistance.

Author Contributions YAG: Conceptualization, Investigation, Methodology, Visualization, Writing—review & editing.

Funding Open access funding provided by the Scientific and Technological Research Council of Türkiye (TÜBİTAK). This work received support from Türkiye Fulbright Eğitim Komisyonu.

Declarations

Competing Interests The authors declare no competing interests.

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