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DIRECT REACTIVE EXTRUSION OF PLA IN THE PRESENCE OF A MULTIFUNCTIONAL CHAIN EXTENDER

Yonca ALKAN GÖKSU[1]*

[1]*Istanbul Technical University, Faculty of Chemical and Metallurgical Engineering, Department of Metallurgical and Materials Engineering, 34469, İstanbul, Türkiye*

Abstract: The environmental impact of non-renewable, fossil fuel-based polymers has led to growing interest in sustainable alternatives such as Poly(lactic acid) (PLA). PLA is biodegradable and suitable for packaging application, however due to limited number of efforts to effectively recycle PLAs, its disposal still contributes to the plastic pollution problem. In general, plastic recycling methods could be categorized into three main groups: (i) incineration for energy generation, (ii) chemical recycling, and (iii) mechanical recycling. Among those strategies, mechanical recycling would be the optimal choice due to its applicability to current plastic production lines. However, limited thermal stability of PLA during melt mixing make its mechanical recycling challenging. This study explores the direct use of ketene-based chain extenders in the melt mixing step without any pre-treatments to enhance PLA's properties during thermal recycling. Those ketene-based chain extenders could increase the molecular weight and hence melt viscosity of PLA by reacting its hydroxyl and carboxylic acid end groups. For this purpose, copolymers of styrene, methyl methacrylate and 2,2,5-trimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione (MA) were synthesized and directly melt mixed with PLA in micro compounder at 210 °C for 3 mins. Force values were monitored simultaneously through this mixing step. Final molecular weights and thermal properties of PLAs were also analyzed through GPC and DSC analyses.

Keywords: Poly(lactic acid), Ketenes, Meldrum's acid, Chain extender, Direct melt mixing

***Corresponding author:** Istanbul Technical University, Faculty of Chemical and Metallurgical Engineering, Department of Metallurgical and Materials Engineering, 34469, İstanbul, Türkiye
E mail: alkanyo@itu.edu.tr (Y. ALKAN GÖKSU)
Yonca ALKAN GÖKSU https://orcid.org/0000-0002-6699-8761

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1. Introduction

Poly(lactic acid) (PLA) is a bio-based polymer that has received considerable academic and industrial attention in recent decades due to its advantageous features for especially food packaging applications (Auras et al., 2004; Rocca-Smith et al., 2017). Lactic acid, the major component, is generated through fermentation from renewable feedstocks such as food crops (corn) and waste sugars (cellulosic material) (Abdel-Rahman et al., 2013; Huysman et al., 2017). While PLA offers the advantage of being derived from renewable sources, its improper disposal keeps contributing to the issue of plastic waste in the environment. Despite the fact that PLA is classified as a biodegradable polymer, that attributes frequently leads to the misperception that this material would degrade quickly in nature (Haider et al., 2019). The degradation of PLA in soil or residential composters requires approximately one year at a temperature of 20 °C, while higher temperatures can expedite the process (Rudnik and Briassoulis, 2011). Investigating the degradation of PLA in marine environments is also a challenging endeavour since factors such as water temperature, salinity, and microbial activity all contribute to the complicated conditions influencing PLA degradation (Bagheri et al., 2017; Atalay et al., 2021).

Indeed, given the time and specific environmental conditions required for PLA to naturally degrade, mechanical recycling emerges as a beneficial alternative in the end-of-life phase. Mechanical recycling involves reprocessing PLA waste to produce new materials, mitigating the environmental impact associated with disposal. This approach not only addresses the challenges posed by the relatively slow degradation of PLA but also contributes to the overall sustainability of the material. By incorporating mechanical recycling into the life cycle of PLA, it would be possible to extend its utility, reduce waste, and foster a more environmentally conscious approach to the management of biodegradable polymers in various industries (Ramos-Hernández et al., 2023).

The reprocessing of PLA through thermal methods poses a significant challenge due to the inherent limitations in PLA's hydrolytic and thermal stability. As the recycling process involves exposure to elevated temperatures, PLA is susceptible to chain scission, resulting in a decrease in its average molecular weight. This chain scission phenomenon is a key factor contributing to the subsequent decline in the mechanical properties of PLA. The compromised molecular structure adversely affects the material's strength and integrity, making it challenging to maintain or reproduce the original mechanical characteristics through thermal reprocessing. Overcoming these challenges necessitates innovative approaches and technologies in thermal recycling methods to minimize the detrimental effects on PLA's molecular structure and preserve its mechanical performance, ultimately enhancing the sustainability of the recycling process for this biodegradable polymer (Liu et al., 2010; Badia and Ribes-Greus, 2016; Beltrán et al., 2018).

Chain extension, a type of post-polymerization modification, involves employing chemical reactions to increase the molecular weight of condensation polymers like PLA. By introducing multifunctional chain extenders during the melt compounding process, it becomes possible to induce chain branching, allowing the modulation of chain length (Meng et al., 2012; Tavares et al., 2016; Grigora et al., 2021; Guclu et al., 2022). Chain extenders consist of two or more reactive chemical functions, such as anhydrides (Piyamawadee and Aht-Ong, 2013; Yahyaee et al., 2020), oxazolines (Berg et al., 2019; Zhao et al., 2019; Karayannidis and Psalida, 2000; Kylmä et al., 2001), isocyanides (Kawashima et al., 2023; Raffa et al., 2012; Tuna and Ozkoc, 2017), and epoxides (Wang et al., 2016; Tuna and Ozkoc, 2017; Al-Itry et al., 2012; Ramos-Hernández et al., 2023). Among these, Joncryl ADR, recognized as a multifunctional styrene–acrylate–glycidyl methacrylate copolymer (Figure 1), stands out as a widely employed chain extender to enhance thermal and mechanical properties of polymers, including PLA (Standau et al., 2022; Kahraman et al., 2023).

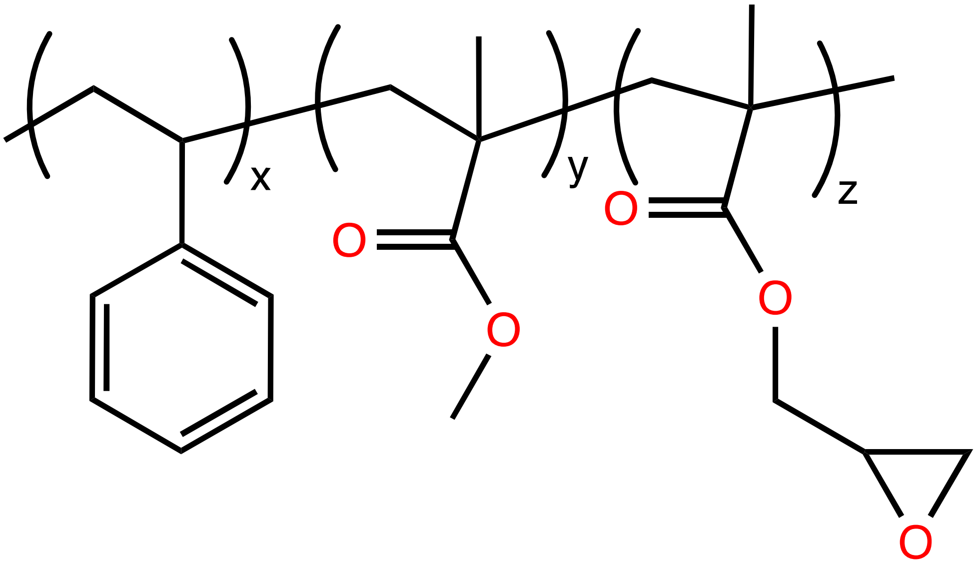

Figure 1. Chemical representation of Joncryl ADR.

The study conducted by Mihai et al. 2010 is noteworthy for introducing branched PLA through the incorporation of Joncryl. According to their results, a notable improvement was observed in shear viscosity and melt elasticity of PLA. The research conducted by Corre et al. (2011) reveal a significant alteration in the molecular weight distribution (MWD) of pure PLA, specifically through the addition of a high molecular weight shoulder indicating the incorporation of longer polymer chains, a result of the chain branching. Jaszkiewicz et al., 2014) investigated the effects of two chain extenders on the melt processing of PLA and found that a masterbatch composed of Joncryl ADR4368 and PLA significantly boosted the molecular weight. Moreover, Joncryl ADR4368 acted as a nucleating agent, leading to improved PLA crystallinity and enhanced mechanical properties, including tensile, flexural, and impact strength. In contrast, Joncryl ADR3229, despite having the same primary structure as ADR4368 but functionalized with maleic anhydride, failed to demonstrate chemical compatibility with the components. Cisneros-López et al., 2020) utilized Joncryl ADR4368 as a chain extender in both virgin and recycled 3D-printed PLA blends. This chain extender effectively curtailed PLA's thermal degradation, enabling improved control over the melt flow index (MFI) and enhancing both storage and loss modulus. Najafi et al., 2012 investigated the impact of three chain extenders—policarbodiimide (PCDI), tris(nonylphenyl) phosphite (TNPP), and Joncryl ADR4368—on the thermal degradation of PLA. TNPP was found to improve the rheological properties, such as viscosity and storage modulus, whereas Joncryl ADR4368 provided even greater enhancement. Meng et al., 2012 evaluated hexamethylene diisocyanate (HDI), Joncryl ADR4368, and pyromellitic dianhydride (PMDA) for their effectiveness in controlling the thermal degradation of PLA. Joncryl ADR4368 yielded the most favorable results, creating a branched and cross-linked PLA structure. This significantly increased the complex viscosity from 4,700 to 23,000 Pa s and provided remarkable thermal stabilization.

Although chain extenders like Joncryl ADR are used to improve the properties of polymers, very recent literature has pointed out that the use of glycidyl methacrylate (GMA) as the functional monomer raises significant health concerns (Aasa et al., 2019; Elkholy et al., 2024). Upon degradation, GMA releases glycidol, a substance classified as carcinogenic by the National Toxicology Program (NTP) (Aasa et al., 2019). This alarming characteristic also necessitates the development of glycidyl-free chain extenders to ensure consumer safety.

In the context of elevating the molecular weight and hence the melt strength of PLA by using glycidyl-free chain extenders, the utilization of ketene intermediates that are highly reactive towards both hydroxyl and carboxyl end groups in PLA might emerge as a promising strategy (Alkan Goksu et al., 2019). Meldrum's acid thermolyses (Figure 2) above 200 °C result in the formation of ketene intermediates, which could readily react with nucleophiles to produce the corresponding esters or amides (Leibfarth et al., 2010; Leibfarth and Hawker, 2013). In our early studies of ketene-based chain extenders, ketene bearing copolymers in the presence of styrene as comonomer were synthesized and these copolymers were blended with PLA through solution casting method to ensure thorough mixing, and then processed in a micro compounder. The GPC results confirmed that the molecular weight of PLA increased when chain extenders were added. Moreover, the incorporation of branching resulted in a noticeable increase in the UV absorption of PLA, indicating potential practical uses in the packaging applications (Alkan Goksu, 2024).

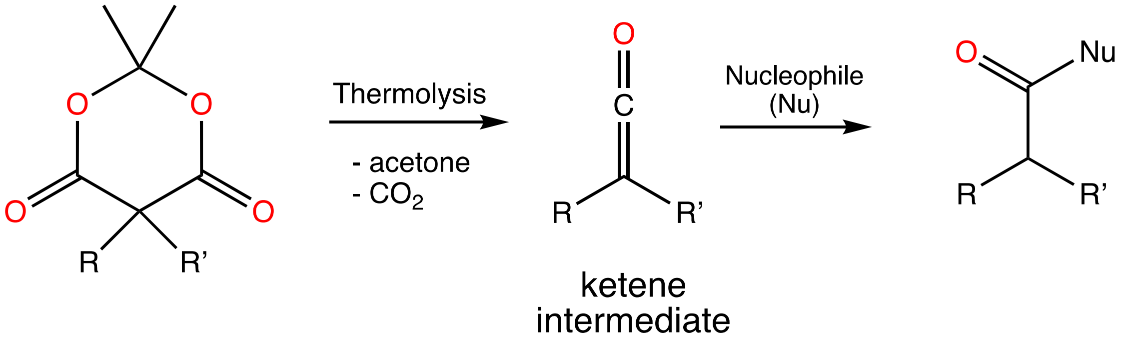

Figure 2. Thermolysis of Meldrum's acid to ketene intermediate, acetone and carbon dioxide.

In order to further enhance industrial processes for ketene-based chain extension, it is definitely more efficient to use direct melt mixing instead of solution casting, as the latter presents challenges when it comes to scaling up. In order to provide a better dispersion of chain extender in the PLA matrix, its chemical structure was redesigned by incorporation methyl methacrylate as a third comonomer and copolymers of styrene, methyl methacrylate and 2,2,5-trimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione were synthesized through conventional free radical polymerization and reactivity of this chain extender towards PLA in molten state without use of any solvent was further investigated. The primary distinctions between the study conducted by (Alkan Goksu, 2024) and the current research are noteworthy and should be highlighted. The earlier solvent casting approach employed by (Alkan Goksu, 2024) has been replaced with a direct melt mixing method, eliminating the need for any solvent. Furthermore, to enhance the compatibility between the chain extender and PLA, the chemical composition of the chain extender has been modified. This modification involved incorporating methacrylic units into the polystyrene backbone previously used in (Alkan Goksu, 2024). Obtained results from current study were compared with the Author's previous study (Alkan Goksu, 2024) and discussed in detail.

2. Materials and Methods

2.1 Materials

The compound 2,2,5-trimethyl-1,3-dioxane-4,6-dione was purchased from Sigma Aldrich and used as is, without any further alterations. Styrene (St, 99% Aldrich) and 1-chloromethyl-4-vinyl benzene (90%, Aldrich) were purified by passing them through a basic alumina column to remove the inhibitor. The following chemicals were used without additional processing: K_2CO_3 (Merck), $NaHCO_3$ (Merck), $MgSO_4$ (Aldrich), Azobisisobutyronitrile (AIBN, 98%, Fluka), acetone (Merck), hydrochloric acid (HCl, 1N, Merck), ethyl acetate (EtOAc, Merck), and hexane (Hex, Merck). The anhydrous N,N-dimethylformamide (DMF) was obtained from the solvent still. The PLA Ingeo 4043D with 94% L-lactide and 6% D-lactide content was sourced from NatureWorks and had a melt flow rate (MFR) of 6 g /10 minutes.

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

4.0 g (26 mmol) of 2,2,5-trimethyl-1,3-dioxane-4,6-dione (MA) and 4.0 g (29.0 mmol) of K_2CO_3 were combined in 80 mL of acetone and stirred for 30 minutes. Then, 1-chloromethyl-4-vinyl benzene (4.0 mL, 28.0 mmol) was slowly added dropwise at room temperature. The reaction mixture was then heated to 55°C and refluxed for 48 hours. After evaporating the acetone under vacuum, the remaining solid was neutralized with 1N HCl and extracted with ethyl acetate (EtOAC). The organic phase was washed successively with water (2 x 50 mL) and saturated aqueous $NaHCO_3$ solution (2 x 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated to yield a yellowish solid. The final product was further purified by column chromatography (using EtOAc/Hex: 1/5 as the eluent, R_f= around 0.3), resulting in 3.1 g (42% yield) of product. The ^{1}H-NMR spectrum (600 MHz, $CDCl_3$, δ, ppm) exhibited peaks at 7.32 (d, J = 7.2 Hz, 2H), 7.15 (d, J = 7.2 Hz, 2H), 6.67 (dd, J=17.6 and 10.9 Hz, 1H), 5.73 (d, J = 17.6 Hz, 1H), 5.24 (d, J= 10.9 Hz, 1H), 3.33 (s, 2H), 1.76 (s, 3H), 1.61 (s, 3H), and 0.98 (s, 3H). In the ^{13}C-NMR spectrum (150 MHz, $CDCl_3$), signals appeared at 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, and 25.71.

2.3. Synthesis of Poly(St-MMA-[1]) copolymer (CE)

Methyl methacrylate (1.2 g, 12 mmol), styrene (1.25 g, 12.0 mmol), [1] (0.73 g, 2.66 mmol), and 2,2′-azobis(2-methylpropionitrile) (AIBN) (45 mg, 0.27 mmol) were dissolved in 4 mL of dry DMF in a Schlenk tube. The mixture underwent three freeze-pump-thaw cycles. Subsequently, the Schlenk tube was immersed in an oil bath preheated to 80 °C and stirred for 4 hours. The resulting polymer was precipitated in cold methanol (1.75 g, 55% conv.).

2.4. Preparation of PLA/CE samples

PLA and CE were pre-blended at various proportions as outlined in Table 1, then individually treated in a micro compounder (Xplore Instruments Micro compounder 5 mL: MC 5) at 210°C and 100 rpm for a duration of 3 minutes.

Table 1. Preparation of PLA/CE Samples

	PLA 4043D (mg)	CE (mg)	CE (wt %)	Conditions
PLA[a]	2000	0	0	
PLA_0.25CE	1995	5	0.25	210 °C, 100 rpm, 3 min, Under N_2
PLA_0.5CE	1990	10	0.50	
PLA_1.0CE	1980	20	1.00	
PLA_2.5CE	1950	50	2.50	
PLA_5.0CE	1900	100	5.00	

[a] PLA directly used

2.5. ^{1}H Nuclear Magnetic Resonance (^{1}H-NMR) analysis

^{1}H-NMR of the synthesized [1] monomer, CE1, PLA, PLA_0.25CE, PLA_0.5CE, PLA_1.0CE, PLA_2.5CE and PLA_5.0CE samples were recorded at room temperature on a Bruker AVANCE III 600 MHz using $CDCl_3$ as the solvent.

2.6. Gel Permeation Chromatography (GPC) analysis

Tosoh EcoSEC Elite GPC system with a TSKgel Super HM-M (17392) column was used for GPC analysis of CE. The column was held at 40 °C and was connected to a refractive index (RI) detector as well as a Tosoh LENSTM 3 multi-angle light scattering detector (MALS). Tetrahydrofuran was used as the mobile phase in this experiment, with a flow rate of 0.5 mL/min. The molecular weight and dispersity values are presented with respect to polystyrene standards. GPC analysis of PLA, PLA_0.25CE, PLA_0.5CE, PLA_1.0CE, PLA_2.5CE and PLA_5.0CE samples were conducted using Waters 2690 Alliance System equipped with two consecutive Polymer Labs PLGel 5 mm Mixed-D and Mixed-E columns with refractive index detection at 35 °C and $CHCl_3$ was used as solvent.

2.8. 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 °C to 250 °C at a heating rate of 10 °C/min. The degree of crystallinity (X_c) of PLA samples were determined using equation (1).

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

Here WPLA is the PLA weight fraction, ΔH_m and ΔH_c are the heat enthalpies of melting and crystallization, respectively. ΔH^o_m is the heat of fusion required to melt 100 % crystalline PLA, which is given as 93.6 J/g.

3. Results and Discussion

To produce chain extender (CE) with Meldrum's acid component, the initial step was the reaction between 2,2,5-trimethyl-1,3-dioxane-4,6-dione and p-chloromethyl styrene (Figure 3). As a result, [1] was synthesized with a moderate yield and it is characterized using ^{1}H-NMR and FTIR analyses and results were reported elsewhere (Alkan Goksu, 2024).

After synthesis and characterization of [1] monomer, its copolymer in the presence of methyl methacrylate (MMA) and styrene was synthesized via free radical polymerization (Figure 4). The obtained GPC results are summarized in Table 2 and ^{1}H-NMR spectrum, shown in Figure 5, confirms the copolymer structure.

The differential scanning calorimetry (DSC) spectra depicted in Figure 6 reveals the thermal behavior of CE. The observed endothermic peak starting at around 190 ^{o}C signifies the heat release during the formation of ketenes, a crucial step in the proposed reaction pathway. The reactivity of these in-situ formed ketene intermediates with the carboxylic and hydroxyl end groups of PLA is a key aspect of the intended chemical modification. This interaction is likely to lead to the desired chain extension and molecular weight increase in PLA, aligning with the overall goal of enhancing the material's properties (Figure 7).

The compounding process of synthesized CE with PLA was executed using a micro compounder set at 210 °C and 100 rpm. Various pre-mixed PLA/CE ratios (0.25, 0.5, 1.0, 2.5, and 5.0 wt%) underwent mixing under these conditions for 3 minutes. The force versus time graphs, as depicted in Figure 8, was obtained during this compounding process. The interaction of mechanical forces in an extruder may reveal important information on the changing mechanical characteristics of the polymer material. When the force values display an apparent increase during the extrusion process, it generally corresponds to a substantial improvement in mechanical strength and resistance, as the polymer experiences a series of structural modifications. The material's improving strength provides an indication of its ability to withstand and adapt to the mechanical stresses and shear forces associated with the extrusion process. The GPC results for neat PLA, PLA processed in the absence of CE under identical conditions, and PLA/CE mixtures have been compiled in Table 3. These GPC findings align seamlessly with the force-versus-time profiles documented during the compounding process, establishing a harmonious correlation between the material's molecular characteristics and its dynamic mechanical behavior. The molecular weight of PLA typically undergoes a decrease during thermal processing in the absence of CE, attributed to bond scission reactions induced by high temperatures and applied shear forces. This inherent characteristic poses a considerable challenge in the thermal reprocessing of PLA. However, a noteworthy breakthrough emerged with the incorporation of CE at a concentration of 0.25 wt%, leading to a substantial increase in the molecular weight. This positive impact on molecular weight indicates the effectiveness of the CE in mitigating the usual degradation associated with thermal processing. Interestingly, with higher CE concentrations of 2.5 and 5 wt%, the observed molecular weight increase is not as pronounced, potentially due to a sudden viscosity surge that hinders further reactions.

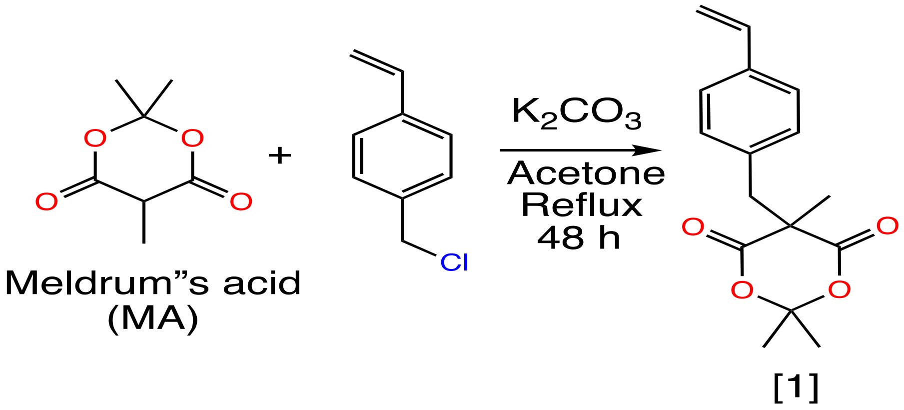

Figure 3. Synthesis of 2,2,5-trimethyl-5-(4-vinylbenzyl)-1,3-dioxane-4,6-dione [1].

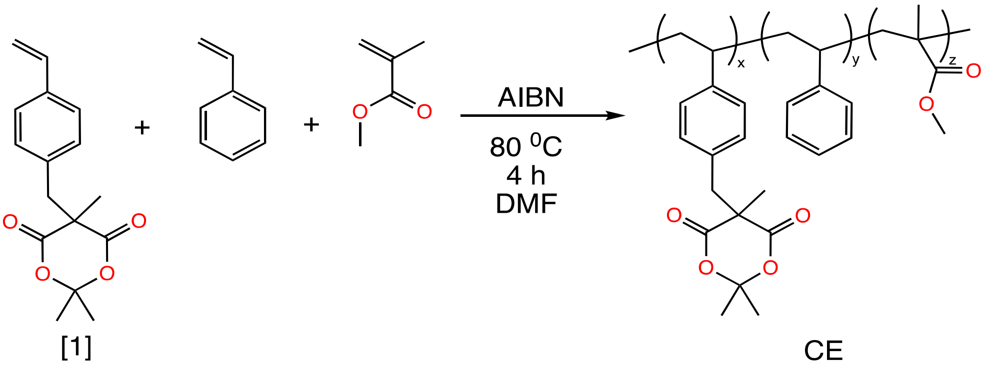

Figure 4. Synthesis scheme of CE.

Table 2. Copolymerization of [1], MMA and Styrene

	Monomer in the Feed (mol%)			Conv.ª (%)	M_nᵇ (kDa)	M_wᵇ (kDa)	PDIᵇ
	[1]	Styrene	MMA				
CE	10	45	45	55	14.9	25.6	1.71

ªOverall conversion was determined gravimetrically. ᵇ Determined by GPC measurements according to polystyrene standards.

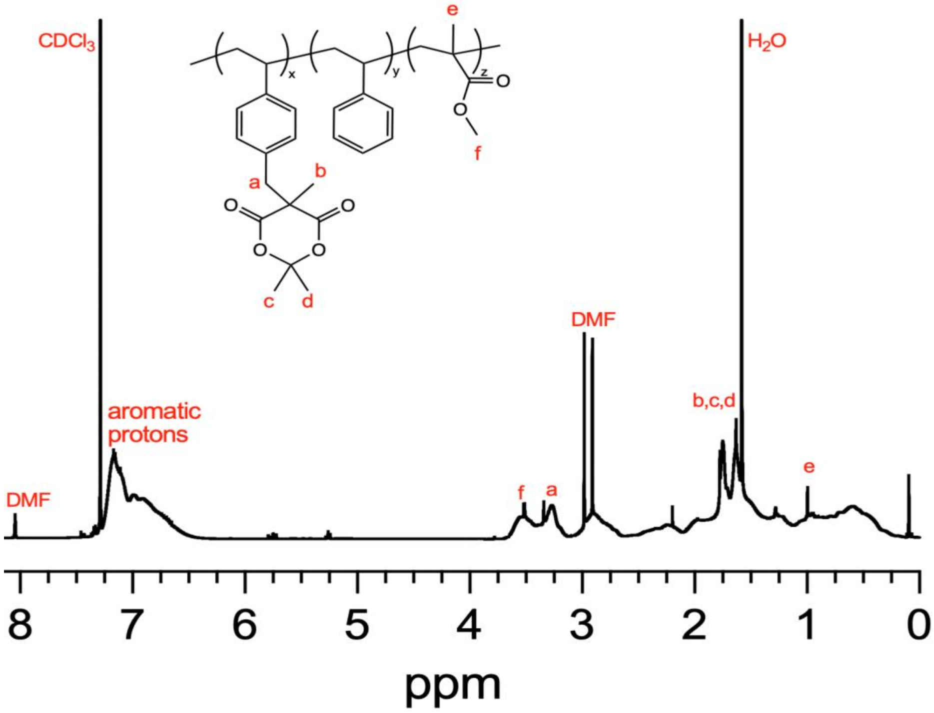

Figure 5. ^{1}H-NMR spectrum of CE.

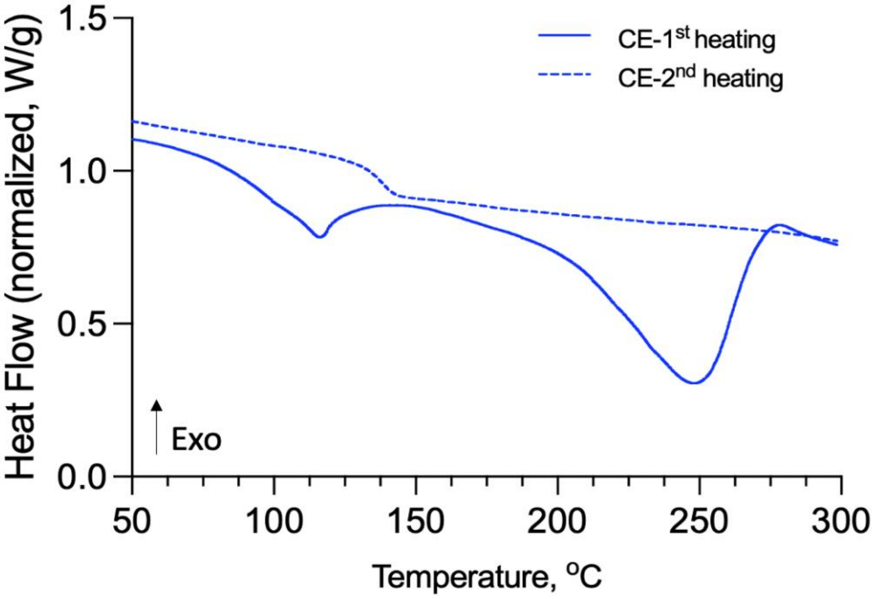

Figure 6. DSC analysis of CE.

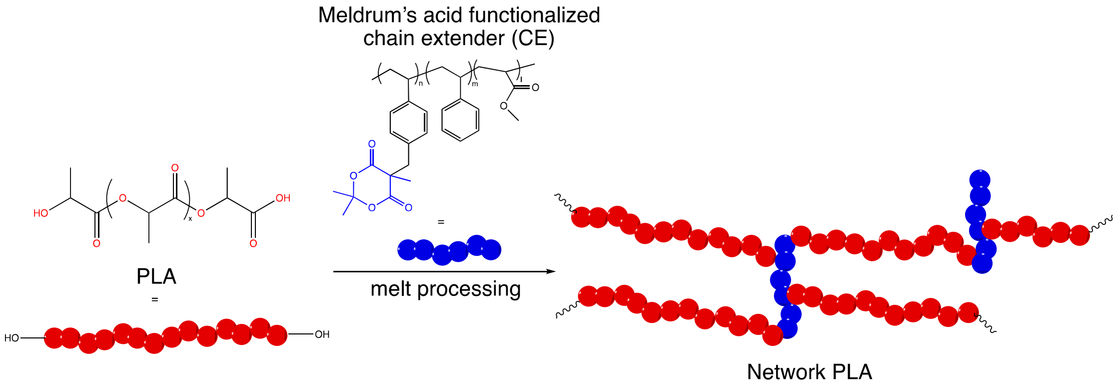

Figure 7. Schematic representation of PLA branching.

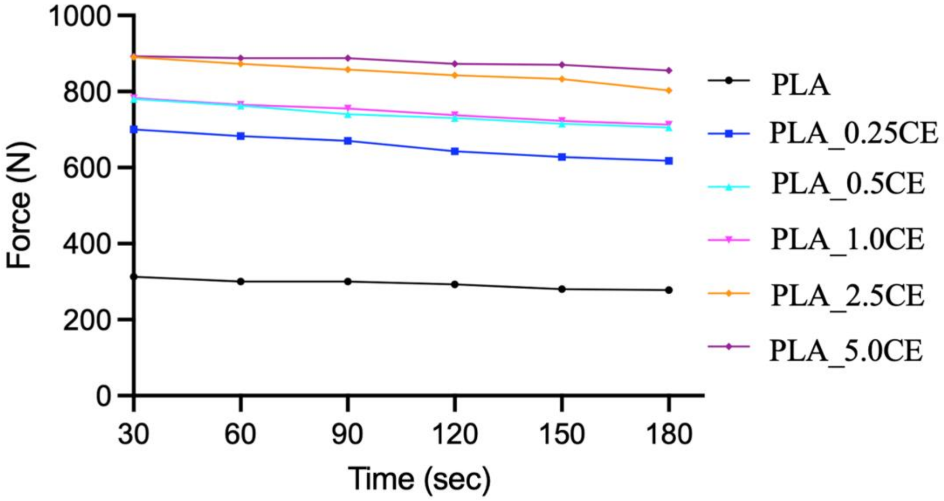

Figure 8. Force vs time graphs of PLA, PLA_0.25CE, PLA_0.5CE and PLA_1.0CE, PLA_2.5CE and PLA_5.0CE.

Table 3. GPC measurements of PLA, PLA_0.25CE, PLA_0.5CE and PLA_1.0CE, PLA_2.5CE and PLA_5.0CE

Sample	M_n[a] (kDa)	M_w[a] (kDa)	PDI[a]
Neat PLA	90.5	140.3	1.55
Processed PLA	66.8	120.1	1.79
PLA_0.25CE	96.6	143.1	1.48
PLA_0.5CE	96.8	141.1	1.46
PLA_1.0CE	108.9	150.2	1.38
PLA_2.5CE	97.5	140.8	1.44
PLA_5.0CE	96.6	137.0	1.42

[a] Determined by GPC measurements according to polystyrene standards and $CHCl_3$ as the solvent.

DSC data of neat PLA, processed PLA and PLA/CE samples summarized in Table 4. In the chain extension process of PLA, glass transition temperature (T_g) undergoes intriguing changes with varying concentrations of the added CE. Specifically, as the amount of CE is increased from 0.25 wt% to 1.0 wt%, there is a consistent decrease in T_g. This reduction in T_g could be attributed to the incorporation of the CE, which likely introduces more flexible segments into the polymer matrix, leading to a decrease in the overall T_g. However, when the concentration reaches 1.0 wt% CE, as T_g begins to exhibit an increase. This sudden rise could be indicative of a complex interplay between the chain extension reactions and the polymer's molecular dynamics. It is reasonable that, beyond a certain threshold, the network formation induced by the chain extender starts to impact the overall structural arrangement, resulting in an elevation of T_g. Simultaneously, the crystallization peak temperature and melting temperature (T_m) display an ascending trend with the addition of CE, suggesting an enhancement in the material's crystalline characteristics. As stated earlier, in our previous research (Alkan Goksu, 2024), copolymers of styrene and [1] in the absence of methyl methacrylate were synthesized, PLA and those chain extenders were dissolved in chloroform to provide and effective mixing. Then, those dried mixtures were fed into micro compounder for 5 mins. Obtained T_m values of 2.5 wt% CE including PLA samples prepared through solution casting (Alkan Goksu, 2024) and direct melt mixing approaches (in these experiments) are 153.9 ^{o}C and 154.9 ^{o}C, respectively. Also, when the T_m values of 5 wt% PLA/CE samples were compared, the value is 150.7 in solution casted samples while 154.4 °C in our current work. Moreover, higher percent crystallinity values are obtained in the present work. These changes might have arisen from the presence of methyl methacrylate unit as a comonomer and the absence of solvent during the pre-mixing step. In other words, incorporation of methyl methacrylate into the chain extender backbone has increased the compatibility between PLA matrix and CE revealing more promising experimental results. Further investigation on the effect of different comonomers in the CE structure on the final PLA properties is an ongoing process in our laboratory.

Table 4. DSC analysis of PLA, PLA_0.25CE, PLA_0.5CE and PLA_1.0CE, PLA_2.5CE and PLA_5.0CE

	T_g (°C)	T_{cc} (°C)	T_m (°C)	χ_c (%)
PLA	56.9	113.2	151.4	1.60
PLA_0.25CE	55.1	118.1	153.2	1.10
PLA_0.5CE	54.9	123.8	154.7	1.74
PLA_1.0CE	56.5	124.4	154.3	1.92
PLA_2.5CE	58.9	124.3	154.9	2.24
PLA_5.0CE	58.3	124.6	154.4	2.79

4. Conclusion

In conclusion, the synthesis and characterization of the CE incorporating Meldrum's acid component have been successfully accomplished. The initial step involved the reaction between 2,2,5-trimethyl-1,3-dioxane-4,6-dione and p-chloromethyl styrene, resulting in the synthesis of [1]. The subsequent copolymerization of [1] with methyl methacrylate (MMA) and styrene (St) via free radical polymerization in the presence of AIBN as radical initiator, produced a structurally confirmed copolymer (CE). The DSC spectra illustrated the thermal behavior of CE, showcasing an endothermic peak around 190°C, signifying the crucial in-situ ketene formation in the proposed reaction pathway. The subsequent compounding of synthesized CE with PLA through direct melt mixing without use of any solvent, as revealed through force-versus-time graphs and GPC results, demonstrated a significant enhancement in molecular weight, particularly with a 0.25 wt% concentration of CE. Moreover, the DSC thermograms of PLA/CE blends exhibited a complex interplay between chain extension reactions and the polymer's molecular dynamics, influencing the glass transition temperature (T_g), crystallization peak temperature (T_{cc}), and melting point (T_m). The study not only advances our understanding of PLA chain extension in the presence and absence of solvent casting treatment but also presents a modular approach to tailor properties by chemically selecting suitable monomers in the chain extender design, offering avenues for optimizing materials for specific applications. Further studies in this line are now in progress.

Author Contributions

The percentage of the author(s) contributions is presented below. The author reviewed and approved the final version of the manuscript.

	Y.A.G.
C	100
D	100
S	100
DCP	100
DAI	100
L	100
W	100
CR	100
SR	100
PM	100
FA	100

C=Concept, D= design, S= supervision, DCP= data collection and/or processing, DAI= data analysis and/or interpretation, L= literature search, W= writing, CR= critical review, SR= submission and revision, PM= project management, FA= funding acquisition.

Conflict of Interest

The author declared that there is no conflict of interest.

Ethical Consideration

Ethics committee approval was not required for this study because of there was no study on animals or humans.

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