# Polymer Chemistry

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# Polymer Containing Lactone Pendant Groups: Synthesis and Potential for Sustainable Materials

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Azra Kocaarslan*[a] and Baris Kumru*[b]

[a]Institute of Functional Interfaces, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen. Karlsruhe, Germany

[b] School of Energy Science and Engineering (ESE), Vidyasirimedhi Institute of Science and Technology (VISTEC), Wangchan Valley, 21210 Rayong, Thailand





## Abstract

The transition from fossil-based plastics to sustainable and circular polymer materials demands not only renewable feedstocks but also chemically diverse structural motifs. Lactones, cyclic esters present in natural products and pharmaceuticals, occupy a privileged position in polyester synthesis. While they are classically exploited as monomers for ring-opening polymerization to polyesters, vinyl-functional lactones and lactone-derived motifs offer a broader design space when incorporated as pendant groups on synthetic polymer backbones. Particularly, the five- and six-membered ring structures of γ- and δ-lactones provide properties like those of acrylate counterparts. Inspired by natural occurrence and developments in biorefinery, lactone pendant group polymers will emerge as attractive functional polymers. In this minireview, we therefore highlight five- and six-membered lactone pendant polymers as an emerging platform for sustainable polymer materials.

## Introduction

Synthetic polymers take place in almost every aspect of modern life, from packaging, coatings and textiles to electronics, energy technologies and aerospace.[1, 2] This versatility, however, comes at a cost. The overwhelming majority of today's polymers are derived from fossil resources which translates into persistent greenhouse-gas emissions across the life cycle and a heavy reliance on non-renewable carbon.[3] Moving towards sustainable polymers therefore requires more than just "drop-in" bio-based monomers: it calls for an integrated approach that couples renewable feedstocks with energy-efficient synthesis and compatibility with circular material flows.

Nature offers a powerful source of inspiration for this transition.[4] Natural macromolecules such as cellulose, starch, chitin, lignin, proteins and nucleic acids demonstrate how complex function can be built from a limited set of simple, renewable building blocks under mild conditions. Cyclic motifs, including sugars, lactones and lactams, are particularly prominent and are used by biology to encode reactivity, recognition and dynamic behavior into macromolecular frameworks.[5] The integration of vinyl polymerization with naturally derived monomers create a powerful platform for designing sustainable, high-performance polymers. Towards this goal lactone-derived vinyl monomers are particularly attractive because they combine a polymerizable carbon–carbon double bond with a cyclic ester functionality in a single molecular structure. In contrast to lactones used directly for ring-opening polymerization, the monomers considered in this review are vinyl-functionalized lactones in which chain-growth polymerization occurs primarily through the C=C bond. This distinction is important: polymerization of the double bond produces carbon–carbon polymer backbones analogous to those obtained from conventional acrylic and methacrylic monomers, while the

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lactone unit is retained as a pendant cyclic ester group. As a result, these monomers offer a route to acrylic-like materials with additional functionality, potential bio-based origin and opportunities for post-polymerization modification through the lactone ring. A representative example is α-methylene-γ-butyrolactone, which can be regarded as a cyclic analogue of methyl methacrylate (MMA). Polymerization through its exocyclic double bond affords polymers with high glass-transition temperatures ($T_g$ around 195 °C), good durability and high refractive indices (1.540), while the pendant lactone ring provides a functional handle for further chemical transformation.[6] Related vinyl lactone monomers have therefore attracted increasing interest as renewable alternatives or complements to petroleum-derived acrylates and methacrylates. Their reactivity, polymerization behavior, and structure–property relationships are strongly governed by the position and substitution pattern of the double bond relative to the lactone ring, distinguishing these monomers from both simple lactones and conventional vinyl monomers.

Thereby this review highlights the potential of lactone pendant polymers and focuses on the synthesis, polymerization and functionalization of lactone-containing vinyl monomers. The particular emphasis is given on the reactivity of the polymerizable double bond and the properties of the resulting polymers bearing lactone pendant groups. Lactones that lack vinyl functionality or are used solely as monomers for ring-opening polymerization are discussed shortly to not to lose sight of strength of respective monomers in ring-opening polymerization (ROP) and direct readers for potential post-polymerization modification strategies.

## 1. Synthesis of Five- and Six-membered Lactone from Bio-sources

Lactones are cyclic carboxylic esters that are typically formed by intramolecular esterification ("lactonization") of hydroxycarboxylic acids, and they occur in ring sizes ranging from strained four-membered β-lactones to five- and six-membered γ- and δ-lactones and up to large macrocyclic systems.[7] This simple motif appears widely in nature, where lactones serve as flavour and fragrance components (for example many γ- and δ-lactones responsible for creamy, fruity aromas such as peach and coconut), pharmacophores in bioactive natural products such as macrolide antibiotics and sesquiterpene lactones [8], and as key signals in chemical communication across insects, vertebrates, and bacteria. For key lactone motifs in natural signalling, we would like to guide readers to review by Schulz and Hoetling, which covers the topic from an organic chemistry aspect. [9] Lactone properties are strongly shaped by ring size and substitution so that ring strain and conjugation control the thermodynamics of ring-opening, while the presence of additional functional groups (e.g.,aromatics alkenes, halogens, or heteroatoms) modulates electrophilicity, hydrolytic stability, and volatility.[10] From a synthetic standpoint, lactones can be accessed not only by classical acid- or base-catalysed lactonization of hydroxy acids, but also via modern methods such as Baeyer–Villiger oxidation of cyclic ketones, transition-metal-catalysed oxidative cyclizations, and halolactonization of unsaturated acids, which together provide broad control over stereochemistry and substitution patterns.[11]

### 1.1 Ring-Opening Polymerization (ROP) of Lactones

Beyond their roles as functional organic building blocks, lactones have emerged as a versatile class of monomers whose ROP provides access to polyesters with finely tunable thermal, mechanical, and degradation profiles. [12] The thermodynamics of lactone ROP are governed primarily by ring strain and substitution pattern. Consequently, the chemical structure of the monomer, the reaction medium, and the nature of the catalyst collectively dictate the position of the polymer-monomer equilibrium and ultimately the attainable molar mass and

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conversion.[13] In practice, a broad toolbox of catalysts is available, including metal-based coordination–insertion systems (e.g. Al, Sn, Zn complexes), organic acids and bases, and bifunctional organocatalysts enabling controlled ROP of diverse lactone families ranging from ε-caprolactone and δ-valerolactone to functionalized lactones and macrolactones, into well-defined polyesters.[14, 15] Complementary to these small-molecule approaches, enzymes such as lipases and cutinases can mediate lactone ROP under mild conditions, offering metal-free, often solvent-lean processes that are attractive from a green chemistry perspective; for a systematic overview of such biocatalytic systems, we refer readers to the review by Kara and co-workers.[16] Another systematic investigation has been reported by Zhao group which examine the polymerization process under different temperatures catalyzed by different types and batches of lipases with various water contents. [17]

In fact, aliphatic polyesters obtained through ROP of moderately strained lactones represent an attractive platform for the development of closed-loop recyclable polymers. In a recent review, Li and co-workers summarized progress in polyesters derived from four-, five-, six-, and seven-membered lactones, with particular emphasis on the thermodynamic and kinetic factors that govern both polymerization and depolymerization. The review also discussed monomer design, polymerization methods, material properties, and strategies for chemical recycling. In this context, the design of lactone monomers is especially important. Suitable structural features must allow the monomer to polymerize efficiently while also enabling the resulting polyester to depolymerize back to the original monomer under appropriate conditions. This balance between polymerizability and depolymerizability is central to the development of closed-loop recyclable polyesters.[18] Within this direction, for instance, Zhu and co-workers demonstrated a benzo-fusion strategy for the design of chemically recyclable semiaromatic polymers. By incorporating a fused aromatic ring into cyclic ester monomers, they showed that monomer structure can be used to tune both the thermodynamics of ring-opening polymerization and the properties of the resulting polymers. [19, 20] These works clearly illustrate how rational monomer design can address the central challenge in closed-loop recyclable polymers by achieving efficient polymerization without sacrificing depolymerizability or material performance. The resulting polyesters can be designed to span from slowly degrading, high-$T_g$ engineering materials to rapidly hydrolysable, bioresorbable matrices for biomedical and packaging applications, which reflect the structural and functional breadth of lactone-based platforms.[18] In a closely related synthetic manifold, polythioesters with distinct degradation behavior and sulfur-containing functionality are accessible via ROP of thiolactone monomers.[21] Given the extensive number of studies and reviews dedicated to lactone ROP, readers are referred to respective works for detailed discussions focusing specifically on ROP methodologies. [22, 23]

In addition to larger lactone derivatives, five-membered ring lactones have also attracted interest as monomers for ROP. Their polymerization generally involves catalyst-mediated ring opening of the cyclic ester, followed by propagation to form the corresponding aliphatic polyester. Scheme 1 illustrates the ring-opening polymerization of α-methylene-γ-butyrolactone, yielding a polyester with pendant double bonds that can be further modified via PPM.

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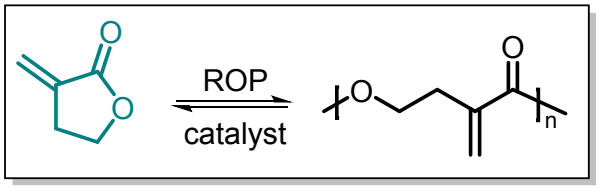
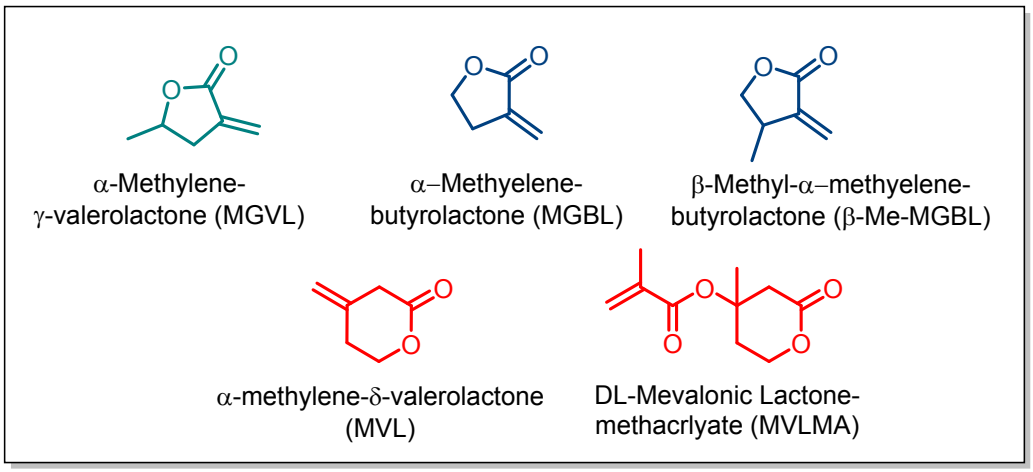



**Scheme 1.** Ring opening polymerization of α-methylene-γ-butyrolactone (MGBL) based on metal-based, organocatalytic and dual catalytic systems. Reproduced from ref 24, published under CC-BY 4.0. [24].

Beyond their role as monomers for ROP, lactones provide valuable functional groups for post-polymerization modification (PPM) reactions. Polymers bearing pendant lactone-derived cyclic ester groups, including γ-butyrolactone-, thiolactone-, and azlactone-based motifs, have been used as reactive platforms for PPM.[24-26] Indeed, the PPM strategy provides access to polymer libraries with tunable chemical composition and material properties without requiring the preparation of a new monomer for each target structure. Therefore, compared with conventional polymers that lack reactive pendant groups, lactone-containing polymers provide an additional level of synthetic flexibility and represent attractive platforms for the development of functional and recyclable materials. Accordingly, ROP methodologies can be exploited as versatile further modification strategies.

## 2. Synthesis of Five- and Six-membered Vinyl Lactone Monomers

Several vinyl lactones that are highly relevant to polymer chemistry originate directly from nature. For example, α-methylene-γ-butyrolactone (MGBL), better known as tulipalin A, occurs in tulips and is formed enzymatically from its glucoside precursor, tuliposide, when bulb scales are damaged or incubated, where it functions as a biologically active defense compound.[27] Another example, mevalonolactone is a six-membered δ-lactone in equilibrium with mevalonic acid, a central intermediate in isoprenoid biosynthesis pathways leading to squalene, cholesterol and a wide range of terpenes.[28]




**Scheme 2.** The most used vinyl lactone derivatives. This review focuses particularly on γ–valerolactone (GVL, green), γ-butyrolactone (GBL, blue), and mevalonolactone (MVL, red) derivatives.

These natural examples clearly illustrate that lactone building blocks can be accessed through biological routes; however, their native abundance is far too limited to serve as realistic bulk

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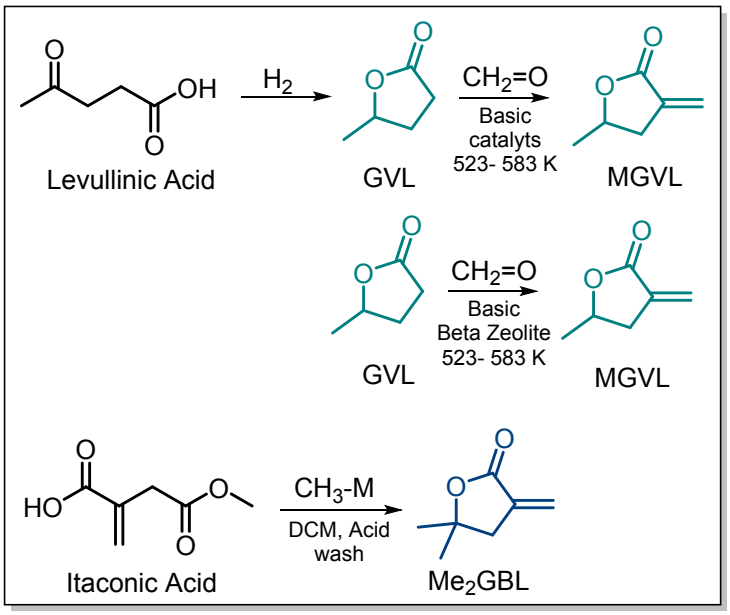
feedstocks for polymer production. Instead, nature offers a conceptual blueprint: lactone-type structures can be obtained at scale via biorefining and biomass valorization.[29] In modern biorefinery schemes, lignocellulosic carbohydrates and other renewable resources are converted into a small set of platform molecules, among which levulinic acid, γ-valerolactone (GVL), γ-butyrolactone (GBL) and itaconic acid are particularly attractive precursors for lactone polymer chemistry. These intermediates can be transformed into vinyl lactone monomers such as α-methylene-γ-valerolactone (MGVL) and α-methylene-γ-butyrolactone (MGBL), providing petroleum-free routes and building blocks suitable for both ROP and vinyl polymerization (**Scheme 3**).[30-35]

The synthesis of MGBL has been demonstrated via enzyme engineering starting from isoprenyl acetate showcasing how pathway design and biocatalysis can open direct selective routes to complex lactone monomers.[36] In parallel, interest in mevalonolactone (MVL) and its parent mevalonic acid has expanded beyond classical isoprenoid biosynthesis: mevalonic acid is now recognized as a key intermediate for bio-based isoprene production which can be upgraded to jet-fuel-range hydrocarbons.[37] Industrial efforts mirror this scientific momentum: the US-based company Visolis produces mevalonic acid and isoprene from biomass at scale, and the FERMEVA project (funded by the Dutch Topsector Energie) brings together multiple industrial partners to establish mevalonic acid synthesis from renewable resources.[38]




**Scheme 3.** Example of synthesis of α-methylene-γ-valerolactone and α-methylene-γ-butyrolactone from levullinic acid and itaconic acid.

Taken together, these developments highlight a clear convergence between biorefinery and polymer chemistry: on one side, intensified efforts to derive lactone-type monomers from renewable carbon; on the other, growing interest in transforming these monomers into sustainable polymers. It is evident that the dynamic equilibrium between lactone formation and hydrolysis is extensively exploited in nature, and that vinyl-functional lactones either occur in biological systems or simply can be accessed via biomass-derived feedstocks.

In fact, considerable interest has been directed toward the development of renewable acrylic alternatives to petroleum-derived methyl methacrylate (MMA). Notably, biomass-derived cyclic analogues, including MGBL, β-Me-GBL, and MGVL, have emerged as promising candidates.[6] For polymer chemists, this offers a clear design cue: lactones can be harnessed as nature-inspired functional pendant groups into robust polymer backbones. In this

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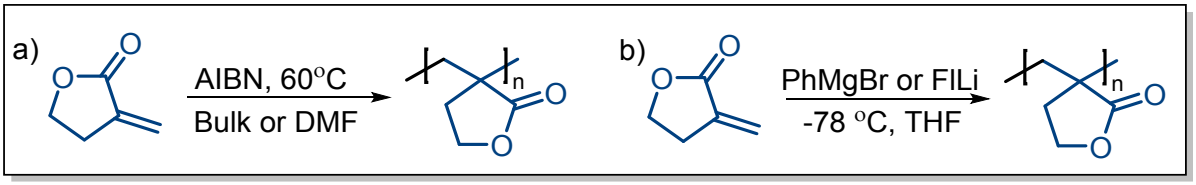
minireview, we adopt a distinct viewpoint on lactones as pendant motifs, surveying the synthetic literature and deciphering the potential of lactone-bearing, renewable polymers for next-generation sustainable and processable materials.

**Table 1** lists the lactone pendant polymers in the literature, including their polymerization strategies and key thermal properties particularly glass-transition temperatures ($T_g$) values. The examples highlight the diversity of accessible architectures from homopolymers to statistical and block copolymers, prepared by free-radical, coordination, living, and photo- or laser-initiated polymerizations, as well as resulting $T_g$ values and processing windows. Collectively, these studies illustrate how the incorporation of lactone side chains influences polymer structure-property relationships while underscoring the breadth of synthetic approaches available for constructing high performance bio-based functional materials.

## 2.2. Synthesis of Five Membered Lactone-Pendant Polymers

### *2.2.1. Free Radical (FRP) and Anionic Polymerization*

MGBL and MGVL are the most studied monomers that afford lactone-functional polymers upon polymerization of vinyl groups. Akkapedi from Allied Chemical Corporation was the first to demonstrate that MGVL is capable of both free-radical (FRP) and anionic polymerization via the vinyl bond in 1979 **(Scheme 4)**.[39] Bulk polymerization was conducted via radical formation using AIBN at 60°C, yielding approximately 70%. Notably, the process exhibits a low E-factor of 0.5, highlighting its high material efficiency. In bulk polymerization of MGVL, however, the reaction exhibits a characteristic limiting conversion because the polymerization mixture vitrifies as the polymer forms. As the $T_g$ of the monomer-polymer mixture approaches the reaction temperature, translational diffusion of monomer and segmental mobility of the growing chain-ends become severely restricted. Consequently, the system becomes glassy, and polymerization is effectively halted, even though the chemical reaction has not yet reached completion ($T_g$ = 195°C). However, this limitation can be overcome by solution polymerization in dimethylsulfoxide (DMSO), yielding a polymer conversion 93%. It should be noted that tacticity refers to the stereochemical arrangement of pendant groups along the polymer backbone, which can strongly influence crystallinity. Consequently, tacticity can have a profound impact on the optical, mechanical, thermal, and chemical properties of a polymer.[40] The final polymer from free-radical polymerization was found predominantly atactic, with only a slight preference for syndiotactic triad placement which significantly lower than that observed for poly (methyl methacrylate) (PMMA). In contrast, anionic polymerization produced predominantly isotactic structures when initiated with either 9-fluorenyllithium in THF or phenylmagnesium bromide in toluene at -78 °C. Later on, anionic polymerization has also been reported using *n*-BuLi and potassium salts in combination with strong, bulky aluminum Lewis's acids.[41, 42]




**Scheme 4.** a) Free-radical and b) anionic polymerization of MBL.

A detailed kinetic study of FRP was conducted in 2015 by Lee and Pitmann on β-Methyl-α-methylene-γ-butyrolactone(β-Me-MGBL).[43] The kinetic study of β-Me-MGBL has shown that

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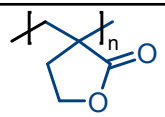
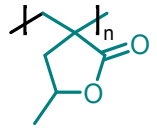
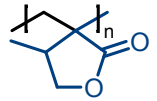
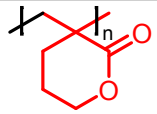
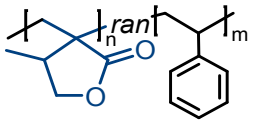
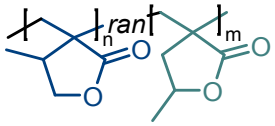
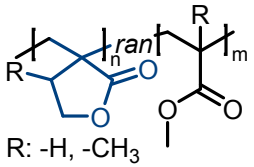
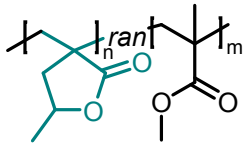
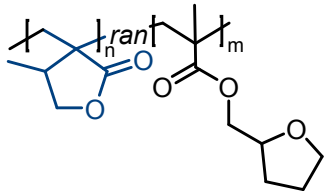
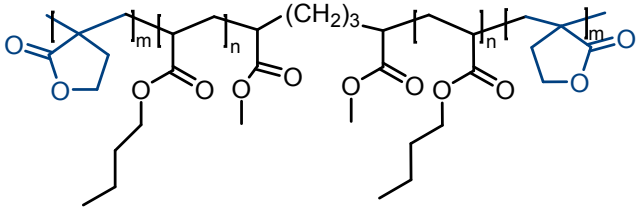
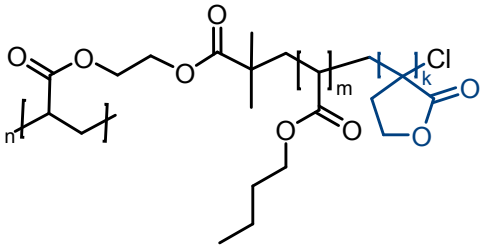
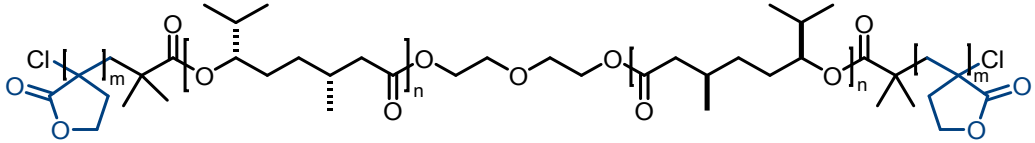
the reaction follows classical free-radical polymerization behavior, with the polymerization rate scaling half-order with respect to initiator concentration and first-order with respect to monomer concentration. The activation energy (~87 kJ·mol$^{-1}$) exceeded that of MMA and related exocyclic methylene lactones, consistent with additional steric constraints during propagation. Although MMA and MGVL are often regarded as structural analogues, MGVL exhibits substantially higher reactivity due to the combined influence of ring strain and the exocyclic double bond. Mälmstrom and coworkers have reported a systematic comparison of MGBL and MA-based acrylic polymers initiated by AIBN and lauroyl peroxide .[44] MBL and MeMBL were successfully copolymerized with MMA and MA using AIBN or LP as the initiator. Monomer incorporation in the resulting copolymers was strongly governed by differences in monomer reactivity ratios, leading to compositional drift in certain systems. These variations in copolymer composition were reflected in the measured $T_g$. For instance, increasing the ratio of PMA in the PMBL-*co*-PMA (3.8:6.2) shifted the $T_g$ value from190 ºC to 138 ºC. Notably, the incorporation of even low amounts of MBL or MGVL markedly enhanced the thermal stability of PMMA and elimante the siccision of head-to-head linkages.[45] The choice of initiator had little effect on polymerization kinetics or final polymer properties under the conditions studied, indicating that monomer structure and reactivity dominate the polymerization outcome.

Klaus and Esposito substantially extended the structure-property relationship of MGVL-derived polymers by examining how different radical polymerization conditions, namely, thermal bulk, photoinitiated bulk, and photoinitiated heterophase polymerization, affect the resulting material properties.[46, 47] Their systematic study demonstrated that variations in initiation mode (thermal- or photochemical), and reaction environment introduce significant and quantifiable changes to molecular weight stability (aqueous heterophase polymerization), thermal degradation behaviour, and $T_g$, even in homopolymers. Thermally initiated bulk polymerization produced the most thermally robust materials across all monomers (MMA, MGVL and styrene (St)) investigated, with decomposition onset temperatures ($T_{dec,on}$) consistently higher than those of polymers formed under photoinitiated conditions. In contrast, heterogeneous photopolymerization yielded materials with substantially reduced thermal stability, attributable to structural irregularities and defect formation arising from the aqueous reaction environment. This effect is particularly pronounced for PMMA and PMGVL, which exhibit lower $T_{dec,\,on}$~80ºC than their bulk-polymerized analogues (e.g., PMMA showing $T_{dec,on}$ values near ~150 °C and polystyrene (PS) ~300 °C), whereas PS shows only modest sensitivity to polymerization method. Differences are also reflected in the $T_g$: averaged across all polymerization routes, $T_g$ values span 106 °C for PS, 116 °C for PMMA, and ~200 °C for PMGVL, demonstrating the intrinsic rigidity imparted by the lactone ring in PMGVL as well as the variation introduced by polymerization history. Overall, these results reinforce a central principle in polymer science: the thermal properties of a polymer cannot be inferred from nominal chemical structure alone but depend on the final polymer structure produced by a given polymerization route. Factors such as temperature, initiation chemistry, and reaction medium may influence thermal properties indirectly by altering molecular weight, chain regularity, branching or crosslinking, end-group composition, and defect concentration.[48]

**Table 1.** Selected Lactone-Pendant Polymers: Polymerization Methods, Conditions, and Thermal Properties.

| Lactone-Pendant Polymer Structure | Notes | Ref. |
|---|---|---|
| **Homopolymers** | | |
|  | Polymerization Methods: Free radical, anionic and coordination, controlled (RAFT) polymerization<br>Thermal Properties: $T_g$ = 195°C for PMGBL and $T_g$ = 225 °C for PMGVL[54] | [39], [41-42], [44], [47], [54], [59-62], [71] |
|  | Polymerization Methods: Free radical, living and coordination polymerization<br>Thermal Properties: $T_g$=199 ± 27.5 °C | [44], [47], [54], [59], |
|  | Polymerization Methods: Free radical and Lewis-pair mediated polymerization<br>Thermal properties: $T_g$ between 206 °C to 220 °C, depending on molecular weight. | [43], [76-78] |
|  | Polymerization Methods: NHC-catalyzed conjugate-addition polymerization<br>Thermal properties: $T_g$=184 | [84] |
| **Random Copolymers** | | |
|  | Polymerization Methods: Free radical, pulsed laser and spontaneous polymerization, photo- (365 nm) and thermal initiation ($T_{poly.}$= 50-70 ºC reaction) | [50] |
|  | Polymerization Methods: Living polymerization<br>Thermal properties: $T_g$= 213 ºC | [49], [53-54], [56], [57], |
|  R: -H, -$CH_3$ | Polymerization Methods: Thermal or photoinitiated free radical, pulsed laser polymerization,<br>Thermal properties: $T_g$= 100-160 ºC. | [50-51], [62] |

| | | |
|---|---|---|
|  | Polymerization Methods: Pulsed laser polymerization/size exclusion chromatography | [51-52] |
|  | Polymerization Methods: Thermally initiated free radical polymerization,<br>Thermal properties: $T_g$=60-130 °C. | [47] |
| **Triblock Copolymers** | | |
|  | Polymerization Methods: Thermally-induced Atom Transfer Radical polymerization (ATRP)<br>Thermal properties: $T_g$= 60-130 °C. | [64] |
|  | Polymerization Methods: Thermal initiated Atom Transfer Radical Polymerization, Star-like polymer<br>Thermal properties: Two distinct Tg, corresponding to the PBA close to −50°C and PMGBL at 195°C segments. | [67] |
|  | Polymerization Methods: Ring-opening polymerization and thermally initiate Atom Transfer Radical Polymerization,<br>Thermal properties: $T_g$=70–190 °C | [68-70] |

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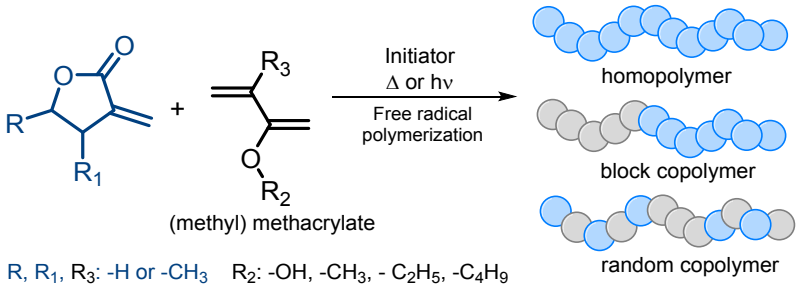
Copolymerization of MGVL and MGBL combines the exceptional rigidity and thermal stability imparted by the lactone pendant groups with the processability and well-established performance of conventional vinyl monomers. A range of polymerization strategies has been employed, including thermal and photochemical initiation, through controlled free-radical, Lewis-pair, and coordination polymerization methods.[49] The first copolymerization study reported by the Akkapedi and coworkers involved free-radical copolymerization of GMBL with MMA, styrene (St), acrylamide (AA), acrylonitrile, and vinylene carbonate, respectively, using AIBN as the initiator at 60°C.[50] Later, Hutchinson and coworkers have studied the copolymerization of MGBL and MGVL with MMA, St and *n*-butyl acrylate (BA) using pulsed laser polymerization/size exclusion chromatography technique.[51] In bulk condition, copolymer composition data are matched to the predictions of the thermal model, excluding MGVL which shows preferential incorporation into copolymers and exhibits kinetic behaviour beyond the simple thermal model.[52]

The further collaboration between Herres-Pawlis and Henkel AG & Co. KGaA led to advances in the copolymerization of bio-derived lactones with established vinyl monomers, most notably acrylate derivatives (**Scheme 5**).[53] The copolymerization behavior of MGBL and its higher homolog MGVL provides a representative case study demonstrating how subtle structural variations in renewable methylene lactones govern their reactivity, sequence distribution, and resulting material properties. In the Q–e framework, MGVL exhibits a significantly higher Q value (3.27) than MGBL (2.48) and a slightly lower polarity parameter (e = 0.61 vs 0.83), indicating an increased radical stabilization imparted by the α-methyl substituent of MGVL. This higher radical reactivity is consistent with the experimentally observed reactivity ratios $r_1$ = 0.63 (MeGBL) and $r_2$ = 1.51 (MGVL), which clearly reflect an alternating tendency between the two lactone monomers. As predicted, such complementary reactivity supports homogeneous copolymer formation with minimal compositional drift. These findings are corroborated by the UV–vis turbidity screening at 450 nm, where poly (MGBL-co-MGVL) copolymers show extremely low absorbance (0.2–0.4 AU), confirming good miscibility and compatibility over a wide compositional range. This behavior stands in strong contrast to acrylate comonomers such as butyl acrylate (BA) or ethylacrylate (EA), whose significant reactivity mismatches lead to pronounced turbidity and phase separation. The MGBL–MGVL pair, therefore, represents a model system in which structural similarity and matched reactivity profiles yield ideal, transparent copolymers.




**Scheme 5.** Schematic illustration of the free-radical copolymerization of vinyl lactones with conventional (meth)acrylate comonomers under thermal or photochemical initiation. Reproduced from ref 53 with permission from American Chemical Society [53], copyright 2025.

Apostolidis and colleagues focused on the polymerization behaviour of these monomers in renewable solvents using AIBN as a thermal initiator [54, 55] . Polymerizations carried out under an inert atmosphere in Cyrene®, GVL, and 2-methyltetrahydrofuran (2-MeTHF) proceeded via solution polymerization, and the polymer was isolated by precipitation into bio-based ethanol.

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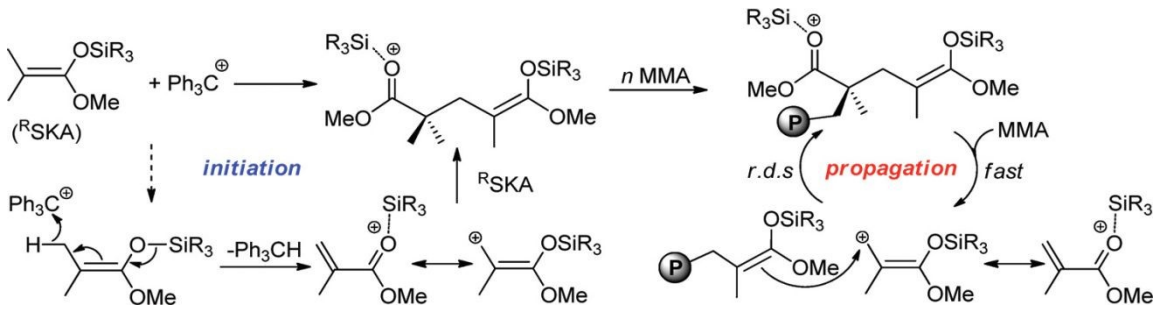
Under these conditions, relatively modest number-average molar masses were obtained ($M_n$ around 5500 g·mol$^{-1}$, $Đ$ = 1.7 at 70% conversion after 5h at 70 °C), resulting in a $T_g$ of 96.4 °C for PGVL. Inspired by the precipitation-based workup, they next explored polymerization directly in a series of bio-based alcohols (1-butanol, 2-phenylethanol, and 1,4-butanediol), which led to precipitation polymerization. In this case, the polymers exhibited significantly higher molar masses ($M_n$ = 27-30 kg·mol$^{-1}$, $Đ$ = 1.4-1.5 at 83–88% conversion after 5 h at 70°C), while the $T_g$ values remained relatively modest (94.7°C for PGBL and 100°C for PGVL), yet comparable to that of a commercial benchmark PMMA prepared by emulsion polymerization (103°C). Films fabricated from the resulting polymer powders showed up to 98% transparency in the visible range (450–700 nm), again matching the optical performance of PMMA. In this setup, AIBN is the only non-renewable component; given its low loading, the overall process, from monomer synthesis to purified polymer powder, relies on more than 99% renewable inputs. Moreover, precipitation polymerization greatly simplifies polymer isolation and allows straightforward reuse of the reaction solvent as well as recycling of the bio-based ethanol used for washing.

### *2.2.2. Living Polymerization*

In all FRP systems, the polymerization of MGBL and MGVL proceeds through the classical termination pathways of radical–radical coupling and disproportionation. The Chen group introduced living polymerization to the MGBL and MGVL using ambiphilic silicon propagating species consisting of both the nucleophilic silyl ketene acetal (SKA) initiating moiety and the electrophilic silylium catalysis (**Scheme 6**).[56] Within the initiation process, they achieved quantitative monomer conversion within 10 minutes at ambient temperature and produced MGVL homopolymers with ultranarrow dispersities ($Đ$ = 1.01, conversion 100%) and predictable molecular weights up to $M_n$ = 31 kg·mol$^{-1}$ with dimethylketene methyl triisobutylsilyl acetal $Me_2C{=}C(OMe)OSi(^iBu)_3$ ($^{iBu}$SKA) initiator. The system also enabled the synthesis of well-defined block and statistical copolymers. Thermal analysis revealed exceptionally high $T_g$ characteristic of butyrolactone-derived polymers, with $T_g$ = 194 °C for PMGBL and $T_g$ = 225 °C for PMGVL, while block PMGVL-*co*-PMGBL copolymer displays two distinct $T_g$ (199°C and 211°C) and random copolymers showed a single $T_g$ around 213°C. Overall, the work represents a major advance in the controlled polymerization of bio-derived vinylidene monomers and provides a mechanistic foundation for engineering next-generation sustainable acrylic analogues.




**Scheme 6.** Living/controlled (meth)acrylate polymerization catalyzed by siliy ketene acetal. Reproduced from [56] published under CC-BY license.

Later, Chen group first attempted to provide a living character to the polymer chain via Lewis-pair polymerization using N-heterocyclic carbene/$B(C_6F_5)_3$ initiators while avoiding chain termination.[57, 58] They achieved exceptionally rapid polymerization of the MGBL monomer,

reaching 100% conversion within 1 minute and obtaining polymers with $M_n$=33.300 g·mol-1. While the system demonstrated excellent polymerization activity for MGBL, it fell short of delivering true living polymerization characteristics.[57] Subsequently, the Zhang group demonstrated living polymerization of MGBL with different Lewis pairs.[59] The study reports the first successful living and controlled polymerization of MGBL and MGVL using an *organic Lewis pair (LP)* consisting of tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) and the strong organophosphorus superbase $P(NIiPr)Ph_2$. This borane–phosphine Lewis pair enables exceptionally rapid polymerization, achieving 100% conversion in as little as 30 seconds, with a record turnover frequency (TOF) of 48 000 $h^{-1}$, the highest reported for living MGVL polymerization. The living nature is confirmed by successful multistep chain extension and the formation of well-defined diblock and random copolymers. The resulting polymer architectures translate directly into distinct structure–property relationships: random copolymers exhibit a single intermediate $T_g$ (204 °C), while diblock copolymers display two separate $T_g$s corresponding to PGBL and PGVL domains, evidencing microphase-separated block structures. In a notable scope-extension study, Chen and coworkers demonstrated that a broad range of conjugated polar monomers, including methacrylates, MGBL, AA, and vinyl phosphonates, can be efficiently polymerized using classical and frustrated Lewis pairs based on the strong Lewis acid $Al(C_6F_5)_3$ combined with diverse Lewis bases such as phosphines and N-heterocyclic carbenes, thereby establishing the versatility and mechanistic breadth of Lewis-pair-mediated polymerizations.[60, 61]

Beyond metal-based and controlled radical strategies, N-heterocyclic carbene (NHC) organocatalysis has emerged as an effective metal-free approach for the controlled polymerization of methylene butyrolactones. Highly nucleophilic NHCs, particularly 1,3-di-tert-butylimidazolin-2-ylidene ($I^tBu$), enable extremely rapid conjugate-addition polymerization of MGBL at room temperature, achieving quantitative conversion within minutes and producing polymers with Mn ≈ 70–85 kg $mol^{-1}$ and dispersities around 1.5–2.0. Although initiation is slower than propagation and true living behavior is not maintained at high monomer-to-catalyst ratios due to internal chain transfer, predictable molecular weights, linear $M_n$-conversion relationships at early stages, and efficient chain reinitiation demonstrate a quasi-living, catalytic polymerization regime that is distinct from conventional radical processes.[62]

### *2.2.3. Controlled Radical Polymerization*

Despite their utility, traditional free-radical, anionic, and Lewis-pair polymerizations afford only limited control over chain uniformity, end-group fidelity, and architectural complexity in the resulting polymer. Controlled radical polymerization (ATRP, NMP, and RAFT), however, provides a powerful toolbox for accessing structurally precise macromolecules, allowing deliberate manipulation of molecular weight, dispersity, topology, and functional incorporation.[63] The Matyjaszewski group first reported well-defined diblock and triblock of MGBL polymers through ATRP (**Scheme 7**).[64] MGBL was polymerized using CuBr with 2,2′-bipyridine (bpy) as a catalyst complex and bromopropionitrile (BPN) as initiator in DMF. A small amount of $CuBr_2$ was introduced at the onset of the reaction to enhance the deactivation rate of the radicals generated from the initiator. Under these conditions, the conversion reached 90% within 100 minutes, yielding polymers with $M_n$= 21 kg·$mol^{-1}$, $Đ$=1.09 ($M_{nexp.}$=18.2 kg·$mol^{-1}$). Chain extension using a PMMA-Br macroinitiator successfully produced the PMMA-*b*-PMGBL copolymer ($M_n$ = 14 900 g·$mol^{-1}$) while maintaining control over polymerization ($Đ$ =1.14). The PMGBL-containing triblock copolymers exhibit exceptional thermal stability, with dual glass transitions at -50°C and ~195°C and a rubbery plateau persisting to nearly 200-

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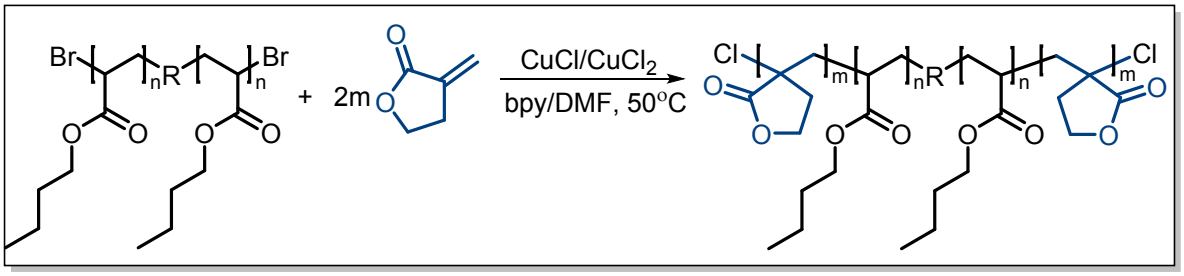
300°C, far exceeding the thermal limits of conventional PMMA-based thermoplastic elastomers.[65] Although PMGBL is often assumed to be a rigid polymer, primarily because of its high $T_g$ (≈ 190°C) and excellent mechanical hardness, Higaki and co-workers applied SEC-MALS and synchrotron SAXS to quantify the intrinsic chain stiffness of well-defined PMGBL, demonstrating that the polymer backbone behaves as a flexible worm-like chain in solution. PMGBL exhibits Kuhn lengths of 1.81 nm in GBL and 1.64 nm in DMF, only slightly larger than those of PMMA and comparable to PS, while its chain diameter (0.80–0.85 nm) also mirrors that of typical vinyl polymers.[66]




**Scheme 7.** Synthesis of PMBL-*b*-PMMA-*b*-PMBL block copolymer thought ATRP. Reproduced from ref 64 with permission from American Chemical Society [64] copyright 2008.

Proposed ATRP methodology also used for creating star-like PBA-*b*-PMGBL block copolymers for high-temperature thermoplastic elastomer applications.[67] Matyjaszewski and coworkers have synthesized the inner soft PBA and outer hard PMBL blocks using a 10-arm and 20-arm PBA macroinitiator at 50°C (**Scheme 8**). A halogen exchange strategy was employed during ATRP of PMBL to achieve cross-propagation rates comparable to propagation rates. Partial star coupling was observed during PMBL block extension from PBA arms, with coupling increasing as the number and length of arms increased. AFM and SAXS analyses revealed phase-separated morphologies, consisting of either hexagonally arranged cylindrical PMBL domains dispersed within a PBA matrix or lamellar structures in samples with higher PMBL content (21–27 wt%). Upon annealing at 230°C, above the $T_g$ of PMBL, a morphological transition was observed in all star-like copolymers, resulting in PMBL cylinders oriented perpendicular to the surface. The dynamic mechanical properties of multi-arm PBA-PMBL block copolymers were characterized by temperature-dependent measurements of the storage (G′) and loss (G″) moduli at a constant deformation frequency of 10 rad/s. Two distinct $T_g$, corresponding to the PBA close to −50°C and PMGBL at 195°C segments, were observed for most copolymers, providing further evidence of microphase separation. The $T_g$ of PMBL became less pronounced as PMBL content decreased and was barely detectable at the lowest PMBL fraction. Dynamic mechanical analysis of multi-arm PBA-PMBL block copolymers revealed two distinct glass transition temperatures corresponding to the PBA and PMBL, confirming microphase-separated structures. As the PMBL content decreased, the PMBL glass transition became less pronounced and was barely detectable at the lowest PMBL content. Noted findings suggest that PGVL-based copolymers could be exploited in specialized high-temperature applications.

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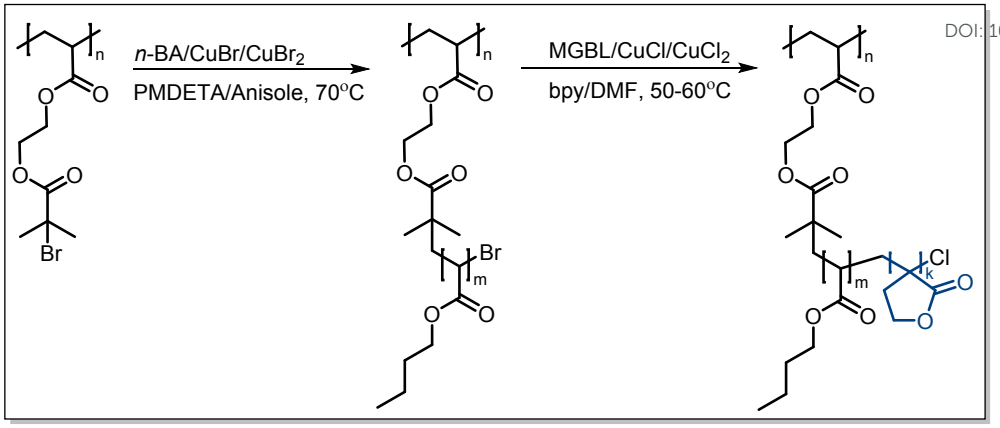
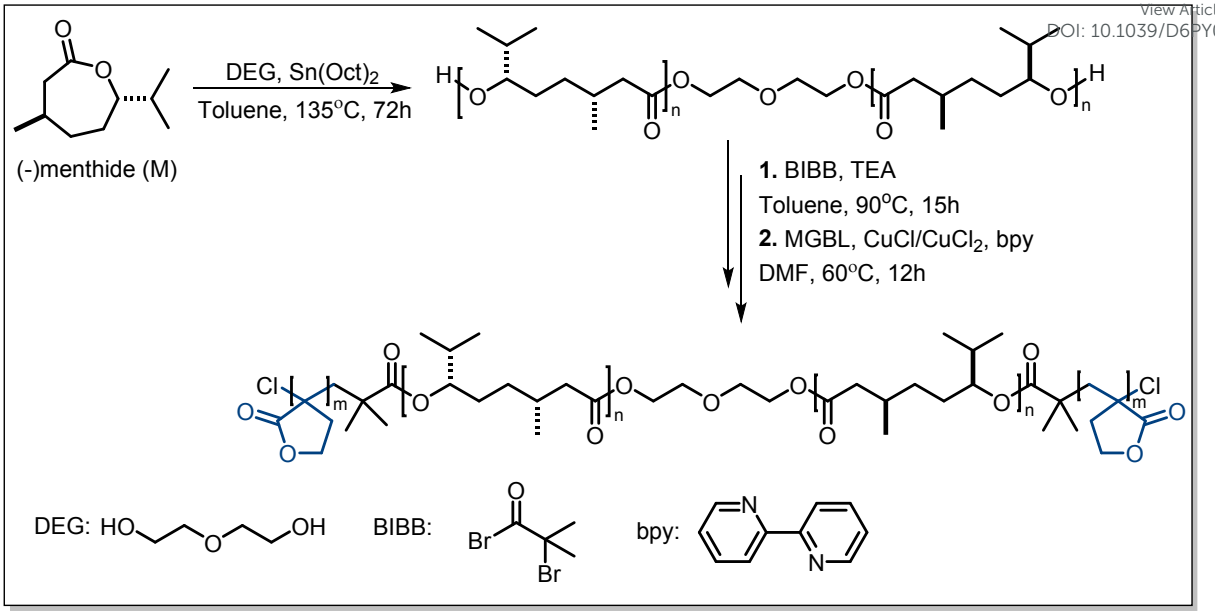



**Scheme 8.** Multi-arm PBA-*co*-PMBL block copolymer synthesis via ATRP. Reproduced from ref 67 with permission from Elsevier [67], copyright 2010.

The Hillmyer group synthesized another thermoplastic elastomer via sequential polymerization of the plant-based monomers menthide (M) and MBL (**scheme 9**). [68] The soft segment has been synthesized through ring-opening transesterification polymerization of menthide (M) using diethylene glycol as an initiator gave α,ωdihydroxy poly(menthide) (HO-PM-OH, $T_g$= -22ºC), which was converted to α,ω-dibromo end-functionalized Br-PM-Br by esterification with excess 2-bromoisobutyryl bromide. The hard segment has been built on this macroinitiator through ATRP. The resulting triblock polymer, PMBL-*b*-PM-*b*-PMB, shows two distinct $T_g$ values as expected, at -21 and 170−190°C, consistent with microphase-separated PM midblock and PMBL end blocks. The triblock copolymer (5–100–5) even maintains exceptional stretchability (>1300% strain) and meaningful mechanical strength even up to 100 °C, demonstrating superior high-temperature elastomeric performance compared with conventional styrenic triblock copolymers, whose elasticity typically deteriorates near their glass-transition temperature. The Hillmyer group has applied this approach to prepare high-pressure-sensitive adhesives from PMBL-*b*-PM-*b*-PMBL renewable triblock copolymers with high $T_g$ values (170-190 °C) via ATRP.[69] Pressure-sensitive adhesives (PSAs) were formulated by blending PMeMBL-PM-PMeMBL triblock copolymers with rosin ester tackifiers (Sylvalite RE-85 and RE-10L). A representative formulation was solution-cast onto PET film and produced a uniform adhesive coating. Adhesion testing showed high peel strength and strong loop tack, indicating excellent immediate and sustained adhesion. Most notably, the formulation exhibited an exceptionally high shear adhesion failure temperature (>150 °C), comparable to cross-linked PSA systems and significantly exceeding the performance of conventional non-cross-linked styrenic block copolymer PSAs.




**Scheme 9.** ABA-type triblock thermoplastic synthesis through subsequent ROP and ATRP from renewable sources. Reproduced from ref 68 with permission from American Chemical Society[68], copyright 2012.

Although ATRP enables well-defined polymer architecture, its reliance on metal complexes can be a limitation. In contrast, nitroxide-mediated polymerization (NMP) offers a metal-free alternative for controlled radical processes. The first successful nitroxide-mediated polymerization (NMP) of MBL was achieved using the alkoxyamine initiator Dispolreg 007 at 80°C in 50 wt% DMSO, targeting $M_n$ 40 kg·mol$^{-1}$. The system exhibited hallmark features of reversible-deactivation radical polymerization (RDRP), including a linear increase of $M_n$ with conversion, early-stage first-order kinetics, and moderate dispersity ($Đ \leq 1.45$). High-end group fidelity was demonstrated through successful chain extension with both St and glycidyl methacrylate (GMA) at 120°C, confirmed by clear GPC shifts to higher molecular weights.[70] Overall, this NMP study highlights the potential of this methodology for creating thermoplastic elastomers, with glassy P(MGBL) end-blocks and a soft rubbery mid-block. Such systems offer a metal-free alternative to ATRP, eliminate catalyst-removal steps, avoid discoloration, and enable the design of high-$T_g$.

However, many attempts to polymerize MGBL and MGVL monomers still rely on using classical organic solvents, with the corresponding, generally high, environmental impact. Picchion and coworkers have demonstrated that the first RAFT polymerization of MGBL can be conducted in supercritical $CO_2$ ($ScCO_2$) using AIBN and 2-cyanoprop-2-yl dithiobenzoate (**scheme 10**).[71] Polymerizations were carried out in a high-pressure Parr batch reactor (max. 350 bar) under nitrogen at 80°C for 24h, yielding polymers with molecular weights in the range of 10-20 kg·mol$^{-1}$ and relatively low dispersities ($Đ < 1.5$). Materials produced in supercritical $CO_2$ exhibited $T_g$ between 155 and 190°C, consistent with the rigid lactone-based backbone. However, it should be noted that residual monomer entrapped within the polymer matrix depresses the measured $T_g$, reflecting plasticization effects associated with incomplete monomer removal. Later, the Hatton group investigated the first MGVL polymerization by RAFT at 80°C in solvents (DMSO, cyrene, t-butanol, and methanol). Purified P(MGVL) homopolymers exhibited high $T_g$ (206-221°C) and excellent thermal stabilities, where the onset of degradation was observed in the region of 345-366°C.[72]

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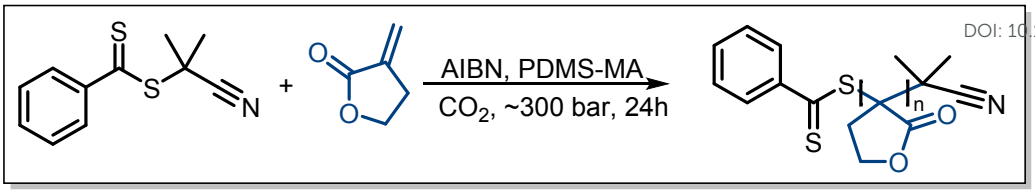


**Scheme 10.** Raft polymerization of MGBL in supercritical $CO_2$ at 300 bar. Rproduced from ref 71 with permission from John Wiley and Sons [71], published under CC BY-NC-ND.

Further studies from the Picchioni group have reported a two-step synthesis of linear PMBL-b-PHMA-b-PMBL copolymers comprising a soft/rubbery poly(n-hexylmethacrylate) (PHMA) inner block and two hard PMBL outer segments via metal-catalyst-free reversible addition–fragmentation chain-transfer (RAFT) polymerization.[73] A two-step RAFT polymerization employing a bis-functional chain-transfer agent enabled precise control over molecular weight ($M_n$= 25-35 kg·mol$^{-1}$), narrow dispersity ($Đ$= 1.1-1.3*)*, and symmetric block growth. By varying the monomer feed during the chain-extension step, the hard/soft block ratio was systematically tuned, allowing direct control over morphology and mechanical properties. SAXS reveals that triblock copolymers form well-ordered microphase-separated morphologies, transitioning from spheres to cylinders and lamellae as PMBL content increases, with domain spacings rising from ~6 to ~42 nm. Sharp higher-order reflections and dual $T_g$ values (PHMA ~5 °C; PMBL ~160–195 °C) confirm strong phase separation and uniform block sizes. In contrast to SBS, whose polystyrene domains lose physical crosslinking near ~100 °C, the high-$T_g$ PMBL domains preserve morphology and physical crosslinks at elevated temperatures, enabling superior thermal stability and reprocessability.

### ***2.2.4. Coordination Addition Polymerization***

In addition to controlled radical approaches, coordination polymerization using sandwich-type (metallocene and lanthanocene) catalysts has also been successfully applied to MGBL and MGVL vinyl monomers.[74, 75] The first study on the coordination-addition polymerization of renewable MGBL and MGVL vinyl monomers has been reported by the Chen group, using neutral lanthanocene(II), non-lanthanocene(III), and cationic group 4 metallocene catalysts **(scheme 11)**. [75] The polymerization of MGBL is initiated by the divalent samarocene catalyst $Cp^*_2Sm(THF)_2$ via an unusual redox-then-radical-coupling mechanism, rather than conventional σ-bond insertion. In the initiation step, Sm(II) undergoes single-electron transfer to the coordinated MBL monomer, generating a radical anion that couples head-to-tail with another radical to form a bimetallic Sm(III)–polymer diinitiator, meaning that two metal centers generate one growing polymer chain. Initiator efficiencies of ~50% evidence this bimetallic initiation under a unimetallic assumption, but around full conversion when a bimetallic model is applied, as well as second-order kinetics in catalyst concentration. This initiation pathway directly impacts the final polymer by enabling living/controlled chain growth, predictable molecular weights that scale linearly with monomer-to-catalyst ratio, narrow molecular weight distributions, and facile block copolymer formation. Moreover, the absence of chain-breaking side reactions during initiation preserves polymer backbone integrity, contributing to the exceptionally high glass-transition temperatures (194-227°C) and thermal stability of PMGBL and PMGBL compared to PMMA synthesized via conventional radical initiation.

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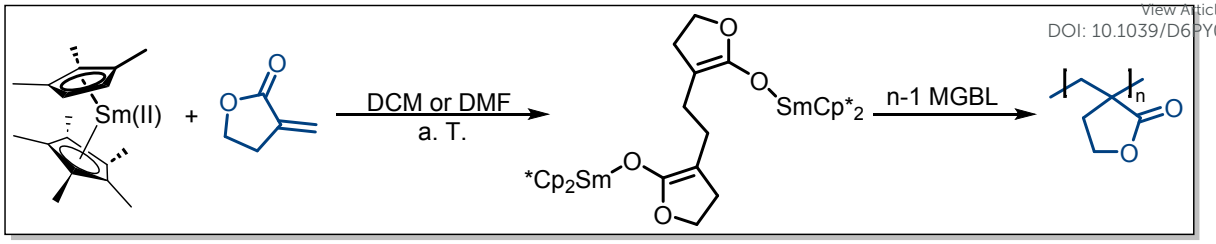


**Scheme 11.** Coordination polymerization of MGBL via metal catalysts (neutral lanthanide and cationic 4 group catalyts) under ambient temperature. Reproduced from ref 75 with permission from Royal Society of Chemistry [75].

Further studies have shown that $C_2$-symmetric zirconocenium (sandwich-type) catalysts and ansa-half-sandwich rare-earth-metal dialkyl and trialkyl complexes can precisely control the stereochemistry of MGBL and MGVL monomers, producing polymers ranging from stereo-random to perfectly isotactic, depending on the monomer structure.[76-78] Further studies have shown that $C_2$-symmetric zirconocenium (sandwich-type) catalysts can precisely control the stereochemistry of MGBL and MGVL monomers, producing polymers ranging from stereo-random to perfectly isotactic, depending on monomer structure. Two catalysts, *rac*-(EBI)$Zr^+$ and *rac*-(EBDMI)$Zr^+$, showed low activity and produced atactic PMGBL (mm ~ 42%, $T_g$ ~195 °C, Mn ~ 17–20 kg·mol$^{-1}$) and atactic PMGVL (mr ~ 42%, $T_g$ ~ 227 °C, $M_n$ ~ 60–65 kg·mol$^{-1}$). In sharp contrast, polymerization of β-Me-MGBL yielded highly isotactic (mm = 95.2%) or perfectly isotactic (mm > 99%) polymers, with quantitative conversion, dramatically enhanced thermal properties ($T_g$ up to 288 °C), and excellent solvent resistance. Computational and experimental data show that steric interactions between the β-methyl substituent, the growing chain, and the metallocene ligand during the initiation/propagation step enforce enantiofacial selectivity, directly translating catalyst structure into polymer stereoregularity and macroscopic performance.

While the use of renewable monomers aligns well with green chemistry principles, the polymerization process itself, as well as the associated separation, purification, and processing steps, play a decisive role in determining the overall environmental footprint of a polymer product. Several studies have therefore focused on tailoring synthetic conditions to maximize the “green” profile of lactone functional polymer materials. Sebakhy and co-workers established a straightforward route to MGBL-based films via initiated chemical vapor deposition, enabling direct polymerization of the monomer in the gas phase onto target substrates using di-tert-butyl peroxide as a free-radical initiator.[79] Experimentally, they correlated deposition kinetics, polymerization rate, and film thickness with thermodynamic parameters and optimized conditions to afford polymer films with an average molar mass of 9200 g·mol$^{-1}$ and a $T_g$ of 164 °C. The coatings exhibited good mechanical robustness as evidenced by nanoindentation measurements, and high optical transparency, with film thicknesses of 2.6 μm and 4.2 μm demonstrated on a range of substrates. In short, this direct film fabrication strategy obviates the need for solution-based film-forming steps and represents a significant sustainability advancement for lactone-bearing polymer coatings.

Towards the goal of improving the polymerization process, Sebakhy and colleagues also reported a horseradish peroxidase-mediated, surfactant-free emulsion polymerization of MGBL in a water/2,4-pentanedione mixture at room temperature (**Figure 1**).[80] Polymerization conducted in air for 3 h resulted in a 98% solid yield and an average molar mass of 73 400 g·mol$^{-1}$, with a relatively high dispersity ($Đ$ = 2.4) for an emulsion system. The presence of air in reaction media accelerated the polymerization process as oxygen plays a key role in active

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radical generation, whereas polymerization under an inert atmosphere took more than 24 hours to be completed. The stable latex displayed an average particle diameter of 131 nm and a high $T_g$ of 200 °C. This approach relies on a simple experimental setup and eliminates the need for expensive inert gas streams that are typically required in free-radical polymerizations. Rapid polymerization in air thus provides a direct and operationally simple route to green MGBL-based polymer latexes.

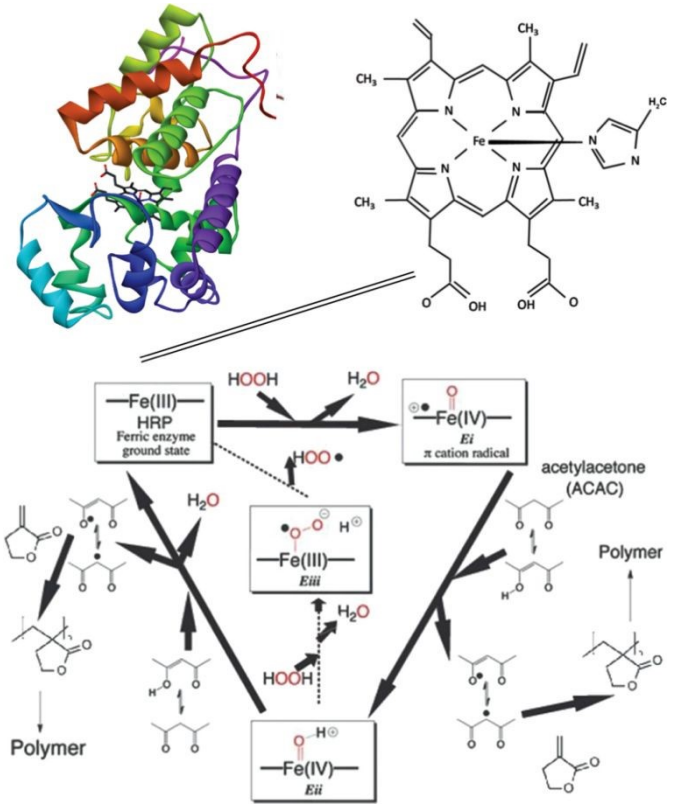


**Figure 1.** Proposed mechanism of surfactant-free horseradish peroxidase-mediated radical polymerization of MGBL in water. Reproduced from [80] published under CC-BY 4.0 license.

### 2.3. Synthesis of Six Membered Lactone-Pendant Polymers

Only a few studies have reported the ROP of mevalonolactone (MVL); in contrast, its methacrylate derivative offers substantial potential as a radically polymerizable monomer to introduce mevalonolactone pendant units into polymer backbones. The monomer is obtained by treating mevalonolactone with methacryloyl chloride in the presence of a base, thereby installing a methacrylate functionality on the hydroxyl group of mevalonolactone. Surprisingly, despite this straightforward synthesis and attractive structure, mevalonolactone methacrylate (MVLMA) has not yet been widely explored by the polymer community, and to date only three publications describe its polymerization and potential applications.

#### ***2.3.1 Free Radical Polymerization***

Just like the polymer of MGBL, which was first reported by industry, the first two reports on the polymerization of MVLMA were published in 1999 and 2001, also by industrial researchers proposing its use in chemically amplified resists for optical lithography. [81, 82] Investigators at AZ Electronics demonstrated free-radical copolymerization of mevalonolactone methacrylate (MVLMA) with 2-methyladamantyl methacrylate (2-MAdMA) in THF using AIBN as the initiator, achieving moderate isolated yields of around 70% (**Figure 2**).[83] The resulting copolymers

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exhibited a $T_g$ of 155 °C determined by modulated temperature differential scanning calorimetry. After polymer characterization, resist formulations were prepared in ethyl lactate, spin-coated, and baked on silicon wafers following standard industrial protocols. Under conventional 193 nm exposure, these resists delivered pattern resolutions down to 130 nm with improved etch resistance relative to the benchmark novolak-based resist.

Subsequently, a similar formulation strategy was explored by Fujitsu.[84] Copolymers with varying MVLMA/2-MAdMA ( 2-methyl-2-adamantane methacrylate, 2-MadMA) molar ratios were synthesized in γ-butyrolactone using 15 mol% AIBN at 70 °C for 8 h. Polymer yields comparable to those in the AZ Electronics study were obtained but significantly lower $T_g$s ranging from 92-105 °C were reported, possibly due to the high initiator loading leading to reduced molar mass. These copolymers were fully compatible with industrial lithographic processes and enabled high-resolution patterning below 100 nm using an ArF excimer laser (193 nm). Collectively, these industry-driven studies show the promise of polymers bearing pendant mevalonic lactone units as high-performance materials for advanced microelectronics and semiconductor lithography.

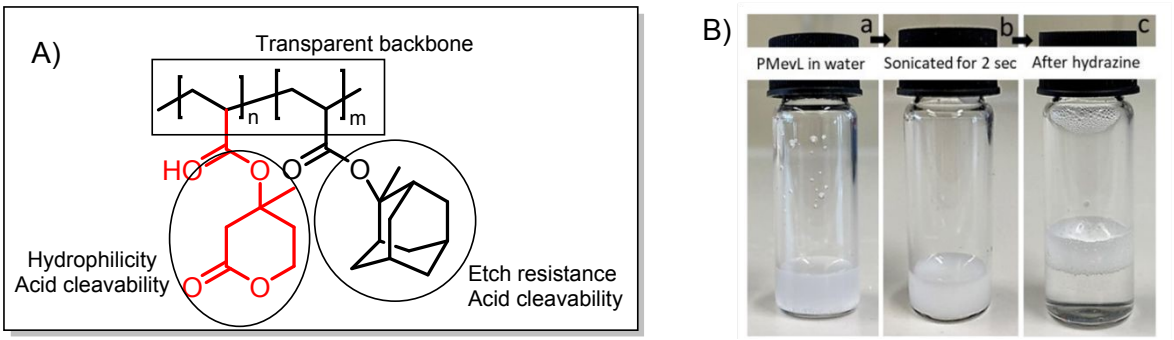


**Figure 2.** A) Structure of MVLMA copolymer prepared by free radical copolymerization used in photoresist applications [84], (B) digital image of MVLMA homopolymer in water and its treatment with hydrazine leading to water soluble polymer formation within seconds. Reproduced from [85] published under CC-BY license.

In 2021, our group adopted an empirical approach to investigate light-induced free-radical and controlled radical homopolymerization of MVLMA, providing the only detailed study on its homopolymer synthesis and properties.[85] We employed the commercial photoinitiator 2,4,6-trimethylbenzoyl diphenylphosphine oxide (TPO), the RAFT agent ethyl 2-(phenylcarbonothioylthio)-2-phenylacetate (dithiobenzoate), and a UV light source (30 W). Conventional free-radical homopolymerization of MVLMA in toluene for 16 h under UV irradiation afforded a white polymer powder in 57% isolated yield after purification, and the polymer structure was confirmed by NMR spectroscopy. Size-exclusion chromatography (SEC) revealed a number-average molar mass of 29 kg mol$^{-1}$ with a $Đ$ of 2.2, and the homopolymer exhibited a high $T_g$ of 154 °C. The material showed high hydrolytic stability with no detectable structural changes after 2 days in $D_2O$. To our surprise, rapid nucleophile-induced ring-opening was observed within seconds accompanied by a notable increase in polymer hydrophilicity. To harness this reactivity, thin films of the homopolymer were spin-coated onto glass substrates; subsequent treatment with hydrazine or thioglycerol led to instantaneous lactone ring-opening and conversion to a hydrophilic surface, clearly demonstrating the responsive character of MVLMA-based polymers. In parallel, we explored photoinduced RAFT homopolymerization which yielded polymer in 20% isolated yield with a molar mass of 7.5 kg·mol$^{-1}$ and $Đ$= 1.5. The living character of this system was confirmed by

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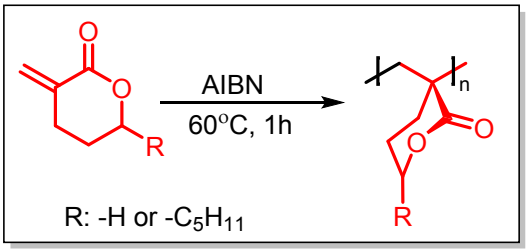
successful chain extension with styrene under light irradiation, although the resulting block copolymer was obtained in only 14% yield. All polymer structures were analyzed and confirmed by NMR spectroscopy, and the (co)polymers were found to be soluble in DMSO, NMP, $CHCl_3$, and DMF. Based on the results, MVLMA is a robust yet underexploited platform for designing nucleophile-responsive, high-$T_g$ materials with significant potential in advanced coatings and functional polymer architectures.

Very recently, Chen and coworkers demonstrated that bio-based α-methylene-δ-valerolactone (MVL) and α-methylene- δ-decalactone (MDL) provide lactone-containing acrylic polymers with both performance and recyclability advantages (**scheme 12**). [86] MVL underwent rapid NHC-catalyzed conjugate-addition polymerization under solvent-free ambient conditions, reaching essentially quantitative conversion within seconds and affording PMVL with *M*n up to $2.0 \times 10^5$ g $mol^{-1}$. PMVL could also be obtained by AIBN-initiated bulk radical polymerization at 60 °C for 1 h. The resulting PMVL displayed a high $T_g$ of 184 °C, compared with ca. 110 °C for atactic PMMA, while PMDL showed a $T_g$ of 122 °C. Despite their high thermal performance, PMVL and PMDL could be selectively depolymerized in bulk under vacuum for 1h at 220 and 210 °C, respectively, affording MVL and MDL in 99.5% and 90% isolated yields. In comparison, PMMA required 400 °C and gave only 53% monomer recovery under the reported conditions. The pendant lactone ring also enabled post-polymerization modification, as partial NaOH-mediated ring opening of PMVL at 80 °C generated water-soluble ionomeric materials. These results highlight the dual role of the lactone unit in vinyl lactone polymers: it enhances thermal and solvent-resistance properties while also serving as a reactive handle for depolymerization, copolymer design, and post-polymerization functionalization.



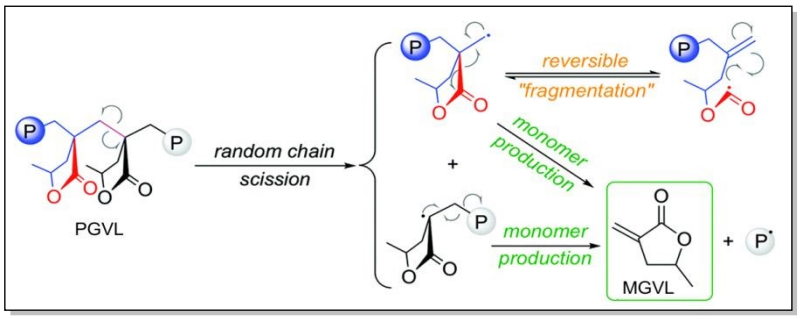

**Scheme 12:** Thermally induced radical polymerization of 6-membered (α-methylene-δ-valerolactone). Reproduced from ref 86 with permission from Elsevier[86], copyright 2024.

### 3. Recycling Potential

ROP of lactones typically yields aliphatic polyesters in which ester linkages are incorporated into the polymer backbone, thereby providing potential sites for hydrolytic degradation or chemical recycling. In contrast, vinyl polymers bearing lactone pendant groups contain the lactone moieties as side-chain functionalities rather than backbone-cleavable units. Consequently, the presence of lactone groups alone does not necessarily impart polyester-like degradability or straightforward whole-polymer recyclability.

In order to assess the chemical recyclability of lactone-bearing polymers, PMMA was benchmarked against PMGBL and PMGVL under identical thermolysis conditions (400 °C, 50 mTorr, 3 h) in simple glassware.[87] Under these conditions, PMMA afforded only ~53% recovery of methyl methacrylate (MMA), with the remaining ~47% of the material converting into intractable carbonized char, whereas the recovered MMA required further purification due to detectable side products. In sharp contrast, PMGBL and PMGVL displayed markedly

enhanced depolymerization selectivity: PMGBL delivered ~65% monomer (MGBL) with the entire mass balance accounted for as volatile monomer plus non-carbonized oligomeric residue ($M_n$~1.5 kg·mol$^{-1}$), while PMGVL reached 76 ± 1% monomer recovery of MGVL, again with the remaining ~24% as oligomer and no char formation. (**Scheme 13**). Notably, MGVL was recovered as a pure monomer. To rationalize this unexpectedly high recyclability, DFT calculations showed that the estimated bulk ceiling temperatures ($T_c$) of PGBL (500 °C) and polyMGVL (405 °C at 9.36 M) are in fact *higher* than that of PMMA (~300 °C), ruling out the low-$T_c$ hypothesis. The tethered five-membered lactone ring stabilizes highly reactive primary macroradicals and suppresses unproductive fragmentation pathways that in PMMA lead to CO/$CO_2$ evolution, char formation, and loss of monomer yield. In short, beyond their renewable feedstock origin, biobased lactone monomers offer attractive process tunability and outstanding chemical recyclability for truly sustainable polymer manufacturing.




**Scheme 13.** The proposed tethering effect of the lactone through thermally induced depolymerization of PMGVL. Reproduced from [87] published under CC-BY license.

The study was supported with DFT calculations which estimated $T_c$ values of MGBL > MGVL > MMA was found consistent with the observed reactivity and polymerizability trend following the same trend. Depolymerization of PMGBL demonstrates improved monomer recovery and reduced carbonization compared to PMMA, although the recovered monomer is not fully spectroscopically pure. The presence of pendant lactone groups appears to suppress side reactions and favor productive unzipping pathways. In contrast, PGVL exhibits higher monomer recovery and purity, which has been attributed to additional γ-methyl substitution that enhances radical stabilization via hyperconjugation. Notably, the residual material from PMGBL depolymerization consists mainly of oligomeric species rather than intractable char, highlighting the potential of lactone-functional vinyl polymers for chemical recycling, while also underscoring the need for further optimization to achieve quantitative monomer recovery.
Another recycling study has been reported by Hong group which stressed out not only post-polymerization modification positibility of lactone monomers also thermal depolymerization profile of these polymers have been achieved with pure monomer recovery.[88] In their study, thermal recyclability of PMGBL was demonstrated using bulk thermolysis under reduced pressure (100 mTorr) in a temperature-controlled furnace equipped with a cold trap to collect volatile products. Depolymerization efficiency strongly depended on temperature, for instance, at 310 °C (slightly above $T_d$), only limited monomer recovery (17.4%) was observed. Increasing the temperature to 330 °C improved recovery to 34.0%, while heating at 370 °C

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enabled quantitative monomer recovery with high purity (GC-MS purity up to 95.7%). The volatile monomer was distilled under vacuum and condensed in the cold trap, confirming complete thermal recyclability under optimized conditions.

To date, reported recycling strategies for such materials have focused primarily on exploiting thermal ceiling temperatures, which holds both the promise and the current limitations of this design approach. However, emerging depolymerization concepts developed in controlled polymerization for PMMA and reversible covalent chemistry may thus provide promising routes for the up- or recycling of lactone-functionalized polymer systems.[89, 90]

**Summary and Outlook**

Lactones are functional cyclic esters that are present in many key biological systems and pharmaceuticals. Functionalized lactones can be obtained from biomass refining to increase their availability for further use. From a synthetic polymer chemistry perspective, lactones are primarily studied as monomers for ROP to afford functional polyesters. However, as explained in detail in this manuscript, their role can be extended beyond ROP when a methylene group is introduced on the lactone building block. To date, lactone-pendant functional polymers have been accessed via a broad range of synthetic methodologies, spanning radical and ionic to coordination polymerization. These studies explore the polymerization behavior of lactone-bearing monomers, evaluate their homo- and copolymerization reactivities, and assess the properties of the resulting materials. Their application potential is often demonstrated through favorable thermal (notably glass transition temperatures, $T_g$) and optical (transparency) properties, positioning lactone-pendant polymers as promising alternatives to poly (methyl methacrylate). In addition, MVL-bearing polymers have been studied for their exceptionally high reactivity towards nucleophiles and for their use as film resists in optical lithography and patterning.

Lactone-functional polymers share an intriguing commonality that the earliest reports of their synthesis originate from industry-affiliated research. Although these studies have not (to the best of our knowledge) yet translated into commercial lactone-pendant materials, they have clearly opened an inspirational pathway for academic research. Despite their frequent association with sustainable polymer design, it is important to recognize that the sustainability advantages of lactone-pendant polymers have not yet been fully realized. In many cases, the employed monomers are still derived from petrochemical sources, and reported recycling strategies often rely on energy-intensive thermal depolymerization processes. As such, the current state of the art should be viewed as a promising platform rather than a fully established sustainable solution.

Looking forward, several key directions can be identified to enhance the sustainability profile of these materials. First, the development of scalable and economically viable routes to bio-based lactone monomers is essential. Although certain monomers such as MGBL (tulipalin A) are naturally occurring, their large-scale production from renewable feedstocks remains limited, and many studies continue to rely on petrochemical synthesis. Advancing biorefinery technologies and integrating partially bio-based carbon sources may provide realistic near-term solutions. Another key prerequisite is transparent reporting on monomer origin. For example, although MGBL is naturally occurring, most studies still employ petrochemically derived MGBL and should therefore not be labelled as “renewable”. Similar considerations apply to other lactone monomers as well. Polymer chemists need to articulate the property and sustainability advantages of these structures clearly enough to justify investment from the biorefinery community in scalable routes, even if only partially bio-based carbon solutions are realistic in the short term.

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Second, as also supported with research studies, rational polymer and monomer design will play a central role in enabling circularity. Tuning ceiling temperatures, incorporating cleavable linkages, or designing systems that respond to orthogonal stimuli could allow for more efficient and selective depolymerization.

Third, improvements in chemical recycling strategies are required. While thermally induced depolymerization based on ceiling temperature concepts has demonstrated the feasibility of monomer recovery, future efforts should focus on reducing energy input and increasing selectivity inspired by current acrylic polymer recycling. The development of catalytic or chemically triggered depolymerization pathways that operate under milder conditions would represent a significant step toward practical closed-loop recycling. In this context, emerging concepts from reversible-deactivation radical polymerization and dynamic covalent chemistry may offer valuable design principles.

Beyond recycling, the intrinsic functionality of lactone units provides opportunities for post-polymerization modification, enabling the design of advanced materials such as drug conjugates, self-assembled systems, and stimuli-responsive architectures. Recent work by Du Prez and co-workers highlights the potential of pendant lactones in dynamic polymer networks, where reversible lactone ring-opening has been used to construct vitrimer systems. [91] Such approaches illustrate how lactone functionality can be leveraged not only for recyclability but also for adaptive and reprocessable materials.

Finally, to substantiate sustainability claims, future studies should incorporate quantitative metrics such as life-cycle assessment (LCA) to benchmark lactone-pendant polymers against established materials. Chen and co-workers reported a techno-economic analysis and life-cycle assessment for the production of PMVL from bio-based sources. [86] Their analysis suggested that bio-based PMVL could become economically competitive with PMMA. The study also indicated that PMVL may offer environmental advantages over PMMA under optimized production and recycling conditions. These benefits were most apparent under ambitious recycling scenarios that exploit the inherent chemical recyclability of PMVL. This example highlights the importance of combining monomer sourcing, recycling efficiency, and LCA when evaluating the sustainability of lactone-based polymers.

In summary, lactone-pendant polymers represent a versatile and conceptually powerful platform at the interface of functional and potentially sustainable polymer design. While significant challenges remain, particularly in monomer sourcing, energy-efficient recycling, and process scalability, continued advances in polymer chemistry and materials engineering are expected to unlock their full potential as components of next-generation circular polymer systems.

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During the preparation of this work, the authors used GPT LLM to enhance language and readability. After using these tools, the authors reviewed and edited the content as needed and took full responsibility for the content of the published article.

**Conflicts of interest**

There are no conflicts to declare.

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No primary research results, software or code have been included, and no new data were generated or analysed as part of this review. All the literature findings can be found in the reference section. The DOI hyperlinks of research and review articles are also amended to the reference section.

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