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RAFT solution polymerisation of bio-based γ-methyl-α-methylene-γ-butyrolactone monomer in DMSO and Cyrene†

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Reversible addition fragmentation chain transfer (RAFT) solution polymerisation of the bio-based lactone monomer γ-methyl-α-methylene-γ-butyrolactone (γMeMBL) has been demonstrated in DMSO and Cyrene. RAFT control was evidenced by control over molecular weights, low disperisites, and kinetic evaluation. Purified P(γMeMBL) homopolymers exhibited high glass transition temperatures (206–221 °C) and excellent thermal stabilities. This work demonstrates the first RAFT solution polymerisation of γMeMBL and the first example of RAFT polymerisation in Cyrene.

Concerns around sustainability of polymers have driven an increase in research into the preparation of new polymers derived from biomass.[1] Recently, interest in a family of five-membered α-methylene-γ-butyrolactone monomers, bearing an exocyclic double bond, has grown as these monomers are analogous to methyl methacrylate (MMA) and can be derived from nature, see Fig. 1.[2,3] For instance, α-methylene-γ-butyrolactone (MBL), also known as Tulipalin A, is found in Tulips. MBL and other analogues, β-methyl-α-methylene-γ-butyrolactone (βMeMBL)[4] and α-methylene-γ,γ-dimethyl-γ-butyrolactone (Me₂MBL)[5] have been synthesised from itaconic acid, an important renewable feedstock converted from glucose.[6] While γ-methyl-α-methylene-γ-butyrolactone (γMeMBL), also known as α-methylene-γ-valerolactone, has been prepared via a γ-valerolactone intermediate from levulinic acid, another biomass derived starting material.[7] Others have also demonstrated the

transformation of γ-valerolactone to γMeMBL in batch[8] and flow reactors.[9]

The versatility of these monomers has been demonstrated through successful anionic, group transfer, free radical, reversible deactivation radical, and ring opening polymerisations.[3,10–13] Ring opening polymerisation results in a polyester containing double bonds,[14] while other polymerisation methods (anionic, radical, group transfer) proceed through the exocyclic double bond, retaining the five-membered ring structure within the polymer.

RDRP techniques such as reversible addition fragmentation chain transfer (RAFT) polymerisation, atom transfer radical polymerisation (ATRP) and nitroxide mediated polymerisation (NMP) have become popular techniques to synthesise well-defined polymers, including various architectures with control over molecular weights.[15,16] The use of these techniques to synthesise new bio-based polymers using monomers derived from renewable resources has grown in recent years.[17,18] However, RDRP investigations of this class of α-methylene-γ-butyrolactone monomers is limited to a few examples. MBL was polymerised by ATRP[19–21] and NMP[22] to generate well-defined homo- and block copolymers and has also been demonstrated in oxygen tolerant photochemically induced ATRP.[23] RAFT polymerisations of these monomers have been investigated in the bulk, solution and miniemulsion polymerisations. Qi et al. reported RAFT bulk and miniemulsion polymerisations of γMeMBL in 2008, using cumyl dithiobenzoate as

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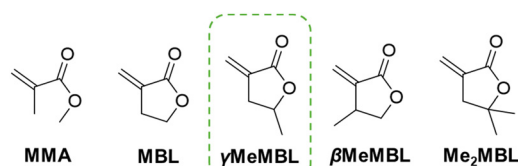Centre for Polymer and Material Technologies (CPMT), Ghent University, Ghent,
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Fig. 1 Chemical structures of MMA and the family of 5-membered α-methylene-γ-butyrolactone monomers; MBL, γMeMBL, βMeMBL and Me₂MBL.

the chain transfer agent (CTA).[24] While this CTA controlled the bulk polymerisations reasonably well, aggregation of latex was observed in miniemulsion. To overcome difficulties with the polymerisation of γMeMBL, styrene was employed as a comonomer. In 2013, Luo and coworkers reported the RAFT *ab initio* emulsion copolymerisation of γMeMBL and styrene, using a poly(acrylic acid)-*b*-(styrene) macromolecular chain transfer agent, reporting latex with up to 60 wt% γMeMBL.[25] Trotta *et al.* have recently demonstrated the RAFT polymerisation of MBL and Me$_2$MBL in benzene, using 2-cyano-2-propyl benzodithioate (CPDB) as the chain transfer agent.[5] Recently, RAFT polymerisation of MBL using CPDB was reported in supercritical CO$_2$ at 300 bar and 80 °C, reporting relatively high conversions (85%) after 24 h, compared with using DMF as the reaction solvent ($\sim$65%).[26] Thus, the RDRP of these monomers is limited and warrants further investigation.

While it is important to use renewable and bio-based materials, it is also imperative to focus on other reaction conditions to improve sustainability by applying Green Chemistry principles.[27] For example, more sustainable solvents reported for RDRP polymerisations include 2-methyltetrahydrofuran,[28,29] ethyl lactate,[30-32] cyclopentyl methyl ether[29,33] and ionic liquids.[34] Cyrene (dihydrolevoglucosenone) is a solvent of interest as it has been reported as an alternative to polar solvents (DMSO, DMF, NMP), can be produced from biomass, is biodegradable, non-mutagenic and non-toxic.[35] Recently, Cyrene has been reported as a suitable solvent for Cu catalysed RDRP polymerisations of (meth)acrylates[36,37] and ring opening methathesis polymerisation of levoglucosenyl alkyl ethers.[38] However, it is still unexplored as a solvent for RAFT polymerisation.

Herein, we report RAFT solution polymerisation of the bio-based lactone γMeMBL in DMSO and Cyrene. Initial RAFT polymerisation conditions were screened, including solvent, CTA, radical initiator, and CTA/In ratio. Once suitable reaction conditions were identified, P(MeMBL)$_x$ homopolymers were synthesised with varying degrees of polymerisation, kinetic experiments were conducted, and resulting polymers were fully characterised to reveal impressive thermal properties.

Initial screening was performed to identify suitable RAFT polymerisation conditions (Table S1, ESI†). In all experiments the targeted degree of polymerisation (DP) was 100, while the CTA, solvent and radical initiator were varied. In all cases the
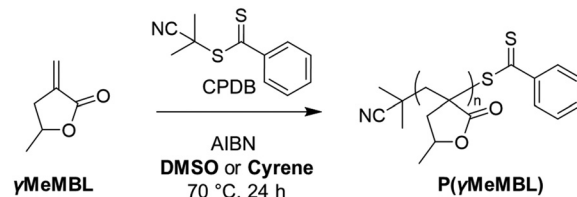
Scheme 1 Reaction scheme for the RAFT solution polymerisation of γMeMBL with either DMSO or Cyrene as the solvent at 70 °C.

monomer conversion, as determined by ^{1}H NMR (Fig. S1, ESI†), was relatively high ($>$85%). Average molecular weights (M_n, M_w) and molecular weight distributions ($Đ$) were determined by CHCl$_3$ GPC analyses. Initially, reaction solvents investigated included DMSO, MeOH and *t*-butanol. DMSO proved to be an effective solvent and has been reported for the free radical polymerisation of γMeMBL previously.[39] Three different CTAs were investigated, CPDB, 4-cyanopentanoic acid dithiobenzoate (CPADB), and 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT). Under identical reaction conditions, CPDB gave a P(γMeMBL)$_{100}$ homopolymer with the lowest dispersity, $Đ$, of 1.26, compared with 1.32 for CPABD and 1.41 for CPDT. Therefore, as CPDB appeared to facilitate the RAFT polymerisation of γMeMBL and gave P(γMeMBL) with a relatively low dispersity ($Đ < 1.3$) compared with CPADB and CPDT, it was used for all subsequent RAFT polymerisations. Previous reports of the RAFT polymerisation of MBL and Me$_2$MBL also used CPDB, albeit in a more hazardous solvent (benzene).[5] Using 4,4′-azobis(4-cyanovaleric acid) (ACVA) as the radical initiator resulted in slightly higher dispersity of 1.37 compared with 1.26 with azobisisobutyronitrile (AIBN), hence AIBN was used for the rest of the study. The selected polymerisation conditions in DMSO are detailed in Scheme 1.

To investigate the RAFT solution polymerisation of γMeMBL further, varying degrees of polymerisation (DP = 50–400) were targeted, see Table 1. The CPDB/AIBN ratio was maintained at 5, and the monomer concentration was 40% w/w. High conversions were obtained when targeting DPs between 50–200 ($>$92%), with a moderate reduction in conversion observed at the highest target DP of 400 (73%), likely caused by the reduced initiator concentration. The resulting P(γMeMBL)$_x$

Table 1 Conversions, theoretical M_n, and M_n, M_w and $Đ$ values by GPC analyses for P(γMeMBL) synthesised by RAFT solution polymerisation in DMSO or Cyrene at 70 °C for 24 h, using CPDB as the chain transfer agent

Target composition	Solvent	Conversion[a] (%)	$M_{n\ th}$[b] (g mol^{-1})	M_n[c] (g mol^{-1})	M_w[c] (g mol^{-1})	$Đ$[c]
P(γMeMBL)$_{50}$		97	5700	5000	6600	1.31
P(γMeMBL)$_{100}$		94	10800	8300	10800	1.31
P(γMeMBL)$_{200}$	DMSO	92	20900	13500	16900	1.26
P(γMeMBL)$_{400}$		73	33000	19800	25100	1.27
P(γMeMBL)$_{50}$		95	5500	5700	7100	1.25
P(γMeMBL)$_{100}$		78	9000	7100	9400	1.32
P(γMeMBL)$_{200}$	Cyrene	83	18800	12200	15100	1.24
P(γMeMBL)$_{400}$		65	29400	18100	22100	1.22

[a] Determined by ^{1}H NMR spectroscopy. [b] Theoretical M_n ($M_{n\ th}$) calculated as follows: $M_{n\ th} = ((M_w\ mon \times target\ DP) \times (Conv/100)) + M_w\ CTA$. [c] Determined by CHCl$_3$ GPC analyses.

homopolymers exhibited reasonably low dispersities ($Đ = 1.26–1.31$), see Fig. S2 (ESI†). Moreover, a linear increase in M_n by GPC was observed *versus* theoretical M_n (Fig. S3, ESI†).

Following the RAFT polymerisation of γMeMBL in DMSO, we investigated the feasibility of performing these syntheses in the more sustainable solvent Cyrene. RAFT polymerisations were conducted in Cyrene using identical reaction conditions to those used in DMSO (see Scheme 1) targeting the same DP range of 50–400, see Table 1. Generally, slightly lower conversions were achieved compared with the equivalent polymerisations conducted in DMSO (65–95%). Control over the molecular weights was observed by GPC analyses (Fig. 2). As observed for the polymerisations in DMSO, the M_n by GPC for P(γMeMBL)$_x$ synthesised in Cyrene increased linearly with theoretical M_n (Fig. S3, ESI†) and dispersities, $Đ$, were relatively low ($Đ \leq 1.32$).

Kinetic evaluations were conducted during the syntheses of P(γMeMBL)$_{100}$ in both DMSO and Cyrene, removing samples periodically to determine monomer conversion and molecular weight evolution during the RAFT solution polymerisation, see Fig. 3. First order kinetics were observed along with a linear increase in M_n with conversion, suggesting RAFT control of the polymerisation under these conditions.

It is worth noting that unreacted CPDB was observed by UV-GPC analyses for all samples (during the kinetic evaluations and varying DPs), which suggests that the CTA efficiency here was not optimal. Nevertheless, the presence of the RAFT end groups were confirmed for all P(γMeMBL)$_x$ homopolymers through GPC analyses, evidenced by the direct overlap of the UV absorption peak for the dithiobenzoate group ($\lambda_{max} = 290$ nm) with the corresponding refractive index signal (Fig. S4, ESI†). Furthermore, the RAFT end group fidelity of P(γMeMBL)$_{50}$ was investigated by chain extension with 50 more units of γMeMBL (Table S2, ESI†). The resulting P(γMeMBL)$_{100}$ was found to have moderate dispersity ($Đ = 1.45$), increased M_n and a clear shift in the molecular weight distribution (Fig. S5, ESI†). Deconvolution of the raw RI detector response showed that approximately 20% unreacted P(γMeMBL)$_{50}$ remained, suggesting a blocking efficiency of ∼80%.

One important feature of α-methylene-γ-butyrolactone-based polymers is their impressive thermal properties,

Fig. 3 Kinetic evaluations of the synthesis of P(γMeMBL)$_{100}$ by RAFT solution polymerisation of γMeMBL at 70 °C in DMSO (closed symbols) and Cyrene (open symbols); (A) conversion (blue circles) and the rate of polymerisation (red triangles) *versus* time, and (B) M_n (purple squares) and $Đ$ (orange diamonds) *versus* conversion. The dashed and dotted lines show the linear increase in M_n in DMSO and Cyrene, respectively.
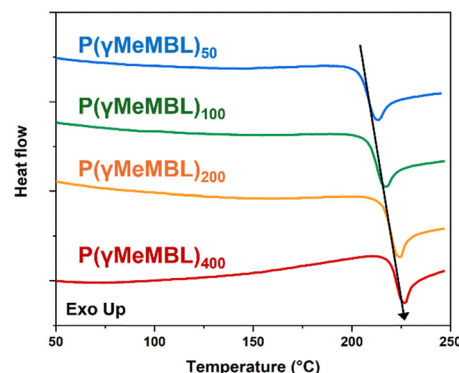
Fig. 4 Offset DSC thermograms for P(γMeMBL)$_x$ synthesised by RAFT solution polymerisation of γMeMBL in Cyrene at 70 °C for 24 h, using CPDB.

compared with PMMA, for example. The P(γMeMBL)$_x$ thermal properties were studied using differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), see Table S3 (ESI†). DSC revealed the polymers exhibited glass transitions, T_g, of 206, 210, 218 and 221 °C for P(γMeMBL) with M_n of 5.7, 7.1, 12.2 and 18.1 kg mol^{-1} respectively, with a molecular weight dependence, see Fig. 4. The increase in T_g with increasing M_n is observed due to the reduction in free volume with increasing chain length, as per the Fox-Flory relationship.[40] Similar T_g values (210–225 °C) were reported by Miyake *et al.*, for P(γMeMBL) synthesised by coordination polymerisation, with $M_n = 2.64–543$ kg mol^{-1}.[41] This represents a marked increase over a typical high T_g methacrylate-based polymer
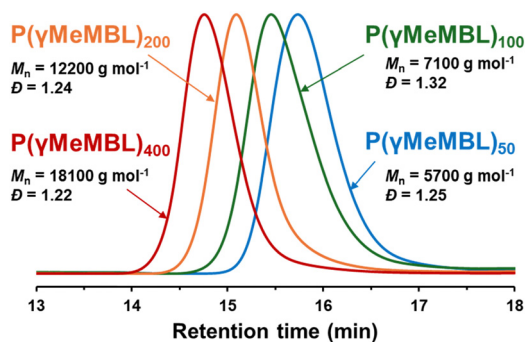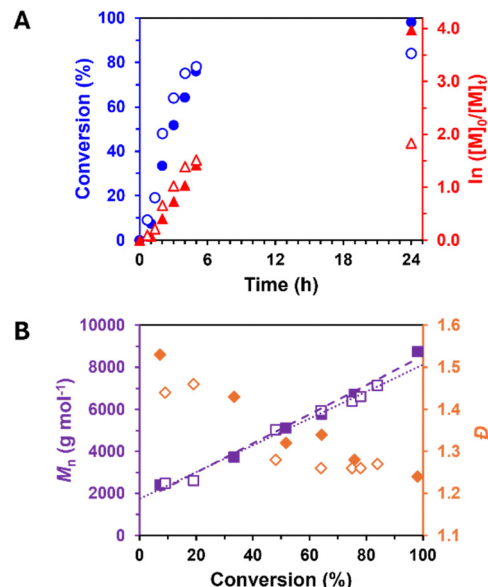

Fig. 2 Normalised overlaid GPC chromatograms for P(γMeMBL)$_x$ synthesised by RAFT solution polymerisation of γMeMBL in Cyrene at 70 °C for 24 h, using CPDB.

poly(methyl methacrylate) (T_g = 105 °C).[42] For all P(γMeMBL)$_n$ samples, a slight endothermic process is also observed towards the end of the T_g step transition, indicative of a enthalpy relaxation.[43] TGA showed that the thermal decomposition of the polymers was nearly identical for all P(γMeMBL)$_x$ compositions, with an onset of degradation observed in the region of 345–366 °C, see Fig. S6 (ESI†). Again, this is appreciably higher than the comparable PMMA (typically in the range of 270–300 °C),[44] and agrees with previous work where the onset of degradation of P(γMeMBL), synthesised by coordination polymerisation, was 356 °C.[45]

In summary, we report the successful RAFT solution polymerisation of the bio-based lactone monomer γMeMBL, and RAFT solution polymerisation using Cyrene, a more sustainable solvent. RAFT control was confirmed by kinetic evaluation, observation of RAFT chain end fidelity and control over target molecular weights and dispersities. However, CTA selection could be improved in future work. The resulting P(γMeMBL)$_x$ homopolymers had high glass transition temperatures ($>$200 °C), with molecular weight dependence observed, and excellent thermal stabilities compared with PMMA. This work demonstrates a move towards both well-defined renewable polymers and more sustainable RAFT polymerisation protocols which are both essential for producing sustainable well-defined polymers for value-added applications.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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