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Mechanochemical ring-opening metathesis polymerization: development, scope, and mechano-exclusive polymer synthesis†

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Ruthenium-alkylidene initiated ring-opening metathesis polymerization has been realized under solid-state conditions by employing a mechanochemical ball milling method. This method promotes greenness and broadens the scope to include mechano-exclusive products. The carbene- and pyridine-based Grubbs 3rd-generation complex outperformed other catalysts and maintained similar mechanistic features of solution-phase reactions. High-speed ball milling provides sufficient mixing and energy to the solid reaction mixture, which is composed of an initiator and monomers, to minimize or eliminate the use of solvents. Therefore, the solubility and miscibility of monomers and Ru-initiators are not limiting factors in solid-state ball milling. A wide variety of solid monomers, including ionomers, fluorous monomers, and macromonomers, were successfully polymerized under ball milling conditions. Importantly, direct copolymerization of immiscible (ionic/hydrophobic) monomers exemplifies the synthesis of mechano-exclusive polymers that are difficult to make using traditional solution procedures. Finally, the addition of a small amount of a liquid additive (*i.e.*, liquid-assisted grinding) minimized chain-degradation, enabling high-molecular-weight polymer synthesis.

Introduction

Ring-opening metathesis polymerization (ROMP) has deeply impacted polymer chemistry by providing a robust synthetic technique for synthesizing functional polymers with wide-ranging applications.[1] Studies on initiator structures, reaction kinetics, new monomers, and reaction conditions have led to dramatic advances in efficiency, selectivity, scope, and applicability of ROMP. Conventionally, most ROMPs have been conducted in the liquid state, with the initiator and monomer reacting in the same phase.[2] When a common solvent is not available, ROMP does not proceed smoothly. Thus, many monomers and the resulting polymers remain unexplored. A new synthetic system not limited by solubility could substantially expand the realm of ROMP.

Mechanochemical synthesis employs chemical transformations induced by mechanical force.[3] Efficient mixing and energy delivery using mechanical methods, such as ball milling, have many merits including solvent-free conditions, less energy input, enhanced reactivity, and unique products.[4] Over the years, mechanochemical syntheses have been successfully established in many areas of chemical synthesis.[5] Mechanochemical polymerization has a long history as well.[6] The first report was the free radical polymerization of vinyl monomers with ball milling by Kargin in 1959.[7] Other critical studies include those by Oprea in the 1970s and by Kuzuya in the 1990s.[8] In the 21st century, green chemistry has become an important topic, and sustainable mechanochemical polymerization has recently received increasing attention.[6] Direct ball milling of reactive monomers has enabled step-growth polymerizations that have produced poly(phenylene vinylene)s, polyphenylenes, polyazomethines, polyurethanes, and polyimides.[9] Mechanochemical chain-growth polymerizations have also been developed, for example, ring-opening polymerizations of lactide and trimethylene carbonate and anion-initiated vinyl polymerization and atom transfer radical polymerization of 2-vinyl naphthalene.[10] These examples have demonstrated that the general merits of mechanochemical synthesis remain valid when applied to polymerizations. However, research on

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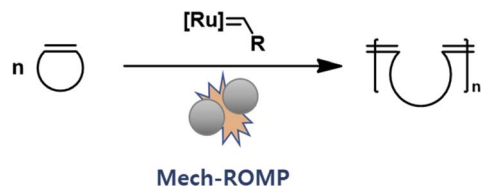
Mech-ROMP

- *Minimal solvent use - Enhancing green metrics*
- *Not limited by monomer solubility*
- *Broad scope*
- *Mechano-exclusive polymers from immiscible monomers*

Fig. 1 Mech-ROMP using ball mill grinding.

mechanochemical polymer synthesis is still in its infancy compared to solution-phase polymerizations. The scope of the reported examples is limited, and the feasibility of many common polymerization techniques under mechanochemical conditions is obscure. Thus, the synthesis of polymers only obtainable by mechanochemical means (*i.e.*, mechano-exclusive polymers) is rarely explored.

Recently, Friščić and coworkers reported that Ru-alkylidene catalysts are active under ball milling conditions for ring-closing and cross-metathesis reactions.[11] Our team envisioned that these catalysts might also be active for the ring-opening reactions required in ROMP. The combination of ROMP and mechanochemistry would improve the greenness of the polymerization and unlock the polymerizations of immiscible monomers, leading to new classes of polymers. Herein, we describe the development and scope of mechanochemical ROMP (Mech-ROMP) (Fig. 1).

Results & discussion

Ru-initiator & ball milling parameter study

A series of representative ruthenium-alkylidene initiators were chosen to conduct Mech-ROMP, including Ru-phosphine (**G1**) and highly reactive Ru–N-heterocyclic carbene (NHC) complexes (**G2**, **G3**, and **HG2**) (Scheme 1). Each initiator (1 mol%) polymerized the model norbornene monomer (**1a**) under solvent-free ball milling conditions (Table 1). Monomer **1a** (50 mg, 100 equiv.) and Ru-alkylidene (1 equiv.) were added into a 10 mL zirconia milling jar with three zirconia balls with a diameter of 8 mm. The tightly closed vessel was placed in a vibratory ball-milling equipment (Retsch MM400). After 30 min at 30 Hz, all

Table 1 Initiator scope in Mech-ROMP[a,b]

Entry	[Ru]	Conv.[c] (%)	M_n^d (kg mol^{-1})	Đ	E/Z[c]
1	**G1**	23	6.4	1.29	76/24
2	**G2**	98	14.1	1.69	57/43
3	**G3**	97	14.5	1.53	57/43
4	**HG**	98	21.3	2.12	57/43

[a] Average values from two experiments. [b] Reaction condition: **1a** (50 mg) and [Ru] = 1 mol% in a 10 mL zirconia jar containing three zirconia balls (8 mm diameter), followed by 30 Hz vibration for 30 min. [c] Determined using ^{1}H NMR spectroscopy. Conv. (%) = a portion of polymeric alkenes of total alkenes. [d] Determined using size exclusion chromatography (SEC) with polystyrene (PS) standards in tetrahydrofuran (THF) at 40 °C.

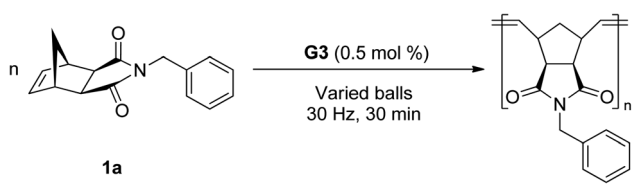reactions were quenched using a few drops of ethyl vinyl ether and milled for 5 min.

The general reactivity trends observed in the solution-phase polymerization reaction were maintained in the solid-state ball milling ROMP.[12] Phosphine-based initiator **G1** exhibited the slowest rate (23% monomer conversion) after 30 min (entry 1), producing the corresponding polymer with a number-average molecular weight (M_n) of 6.4 kg mol^{-1}. **G1** was inactive in the cross-metathesis reaction in Friščić's experiments, which is not the case for ROMP.[11] Highly reactive Ru–NHC species (G2, G3, and HG2) exhibit >90% conversion and high molecular weight (entries 2–4). **G3** with fast-dissociating pyridine ligands showed the narrowest dispersity (Đ = 1.53, entry 2) compared to **G2** (Đ = 1.69, entry 3) and **HG2** (Đ = 2.12, entry 4). **HG2** exhibited a higher M_n than **G2** and **G3** due to slow initiation and fast propagation. The *trans* and *cis* ratios of the product polymers were comparable to those observed in their corresponding solution-phase polymerization reactions.[13] Ru-phosphine **G1** preferably produces the (*E*)-isomer (E/Z = 76/24, entry 1), and the Ru–NHC initiators (**G2**, **G3**, and **HG2**) exhibited near-equivalent E/Z selectivity (E/Z = 57/43, entries 2–4). These results support that mech-ROMP proceeds *via* a mechanism similar to that observed in the solution-phase ROMP.
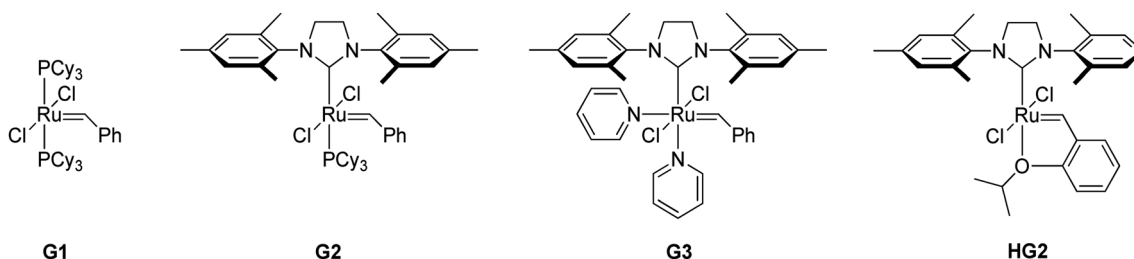
Scheme 1 Structures of Ru-initiators used in this study.

Table 2 Effect of the ball milling parameters[a,b]

Entry	Balls	Conv.[c] (%)	M_n[d] (kg mol^{-1})	Đ[d]
1	8 mm × 1	87	24.1	1.64
2	8 mm × 3	90	22.6	1.67
3	8 mm × 5	93	23.0	1.65
4	10 mm × 1	98	16.5	1.65
5	5 mm × 12	16	N/A	N/A
6	3 mm × 20	<5	N/A	N/A
7	8 mm × 3 (20 Hz)	20	N/A	N/A

[a] Average values from two experiments. [b] Reaction conditions: **1a** (50 mg) and **G3** in a 10 mL zirconia jar, followed by 30 Hz vibration for 30 min. [c] Determined using ^{1}H NMR spectroscopy. Conv. (%) = a portion of polymeric alkenes of total alkenes. [d] Determined using SEC with PS standards in THF at 40 °C.

Next, ball milling parameters were investigated (Table 2). Considering that long polymer chains would undergo chain degradation under mechanochemical ball milling conditions,[14] [M]/[G3] = 200 conditions were used to evaluate both the polymerization and competing chain degradation. Changing the number of milling balls was not a regulating factor (entries 1–3). Ball milling with one 8 mm ball converted 87% of monomer **1a** to the polymer (entry 1). Three and five 8 mm balls resulted in 90 and 93% conversion, respectively (entries 2 and 3). Similar molecular weights were obtained regardless of the number of milling balls used (M_n = 24.1 kg mol^{-1}, 22.6 kg mol^{-1}, and 23.0 kg mol^{-1}, respectively). However, variations in the ball size presented a pronounced effect on the polymerization. Changing to a heavier 10 mm ball resulted in the full consumption of the monomer (entry 4), whereas the use of 5 mm balls (×12) only gave a 16% turnover (entry 5), and 3 mm balls (×20) showed almost no conversion (entry 6). As seen in ring-opening lactide polymerization,[10a] the importance of the collision energy on the reaction efficiency was again confirmed in Ru-ROMP. However, high-energy ball milling enhanced the degree of chain degradation. Specifically, the experiment using a 10 mm ball produced a polymer product with a lower M_n, despite high monomer conversion, than that obtained under 8 mm ball conditions (16.5 vs. 24.1 kg mol^{-1}, respectively). This observation is consistent with Choi and Peterson's results of decreasing degradation kinetics as the ball size decreases.[14a] The effect of the vibration frequency was evaluated (entry 7). A slower vibration (20 Hz) provided poor mixing and low-energy delivery, resulting in a low conversion (16%). These results also rule out the possibility of significant background polymerization not induced by ball milling.

The temperature variation in each reaction was monitored to determine the reaction phase. The ball milling equipment was placed in an isotherm container at 30 °C, which is the initial reaction temperature. At the end of the reaction, the temperature of the reaction mixture was measured using an IR thermometer and was found to have increased to 45–50 °C; these temperature were much lower than the melting point of monomer **1a** (104 °C) and the glass transition temperature (T_g) of its resulting polymer (116 °C). The reaction mixtures at low, medium and high conversions did not exhibit any eutectic state. These observations indicate that the polymerization proceeds in the solid-state.
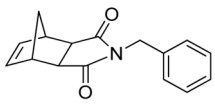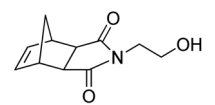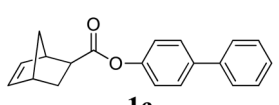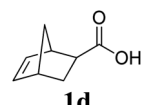
Scope of monomers
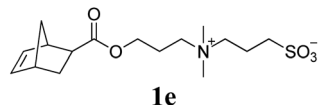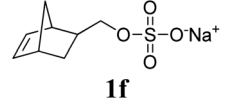
A variety of solid monomers were evaluated under the Mech-ROMP conditions (Table 3). The high functional group compatibility of the Ru-alkylidene initiator was also observed in the solid-state ROMP (entries 1–4). Initiator **G3** maintained its metathesis reactivity in the presence of highly concentrated hydroxy (**1b**), ester (**1c**), and carboxylic acid (**1d**) groups (entries 2–4). ^{1}H NMR and SEC confirmed high conversion and high molecular weight product formation.

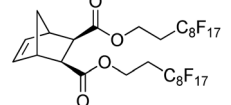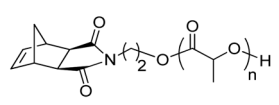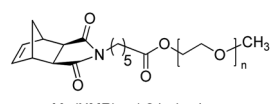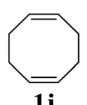Next, the polymerizations of ionic monomers were investigated (entries 5 and 6). Several ROMP examples of ionic monomers in aqueous media have been previously reported.[15] However, modification of the Ru initiator with highly polar pendants was required to make it soluble in water. Mech-ROMP of ionic monomers **1e** and **1f** without a liquid additive resulted in diminished conversions (86 and 9%, respectively) and low molecular weight products (M_n = 5.4 and 4.7 kg mol^{-1}, respectively). In our previous lactide polymerization study, liquid-assisted grinding (LAG, in which a small amount of liquid is added) facilitated the polymerization and retarded polymer chain scission under ball-milling.[10,16] For the Mech-ROMP with the liquid additives of **1e** and **1f**, LAG exhibited positive effects. The unmodified **G3** initiator gave excellent efficiency (99% monomer conversion) in polymerizing ionic monomers **1e** and **1f** with high molecular weights (M_n = 24.7 and 57.5 kg mol^{-1}, respectively) and narrow dispersity values (Đ = 1.36 and 1.32, respectively) with water or dimethylformamide (DMF) assisted grinding (η = 0.4 μL mg^{-1}).[16]

The production of a fluorous polymer was also achieved (entry 7).[17] The LAG of **1g** and **G3** with a 1 : 1 mixture of THF and $C_4F_7OCH_3$ (HFE) (η = 0.4 μL mg^{-1}) provided sufficient mixing, and the corresponding fluorous-polymer was obtained quantitatively. Another interesting class of monomers, norbornenyl-terminated macromolecules (NB-MM), could also be polymerized (entries 8 and 9) with Mech-ROMP, giving bottlebrush polymers.[18] The excellent catalytic efficiency of **G3** in the grafting-through polymerization of NB-MM was sustained under solid-state conditions. Representative norbornene-terminated poly(lactic acid) (**1h**) and poly(ethylene glycol) (**1i**) macromonomers were efficiently polymerized using THF-LAG (η = 0.4 μL mg^{-1}). Cyclooctadienen (**1j**) is a class of ROMP monomer for highly regulated polybutadiene synthesis. Mech-ROMP of **1j** was also successful (entry 10). The fast second metathesis reaction under highly concentrated conditions resulted in predominantly trans poly(cyclooctadiene) (M_n = 26.3 kg mol^{-1}, 92% trans) and a broad dispersity (Đ = 2.48).

Table 3 Scope of the monomers in Mech-ROMP[a,b]

Entry	Monomer	[M]/[G3]	LAG	Conv.[c] (%)	M_n (kg mol^{-1})	Đ
1	**1a**	100	None	97	14.5[d]	1.53[d]
2	**1b**	100	None	98	69.9[e]	1.73[e]
3	**1c**	100	None	91	18.2[d]	1.54[d]
4	**1d**	100	None	98	N/A[f]	N/A[f]
5	**1e**	100	None	86	5.4[g]	1.13[g]
			H$_2$O ($\eta = 0.4$)	99	24.7[g]	1.36[g]
6[h]	**1f**	100	None	9	4.7[g]	1.03[g]
			H$_2$O ($\eta = 0.4$)	54	44.7[g]	1.41[g]
			DMF ($\eta = 0.4$)	99	57.5[g]	1.32[g]
7	**1g**	50	THF/HFE[d] (1 : 1) ($\eta = 0.4$)	99	N/A[f]	N/A[f]
8[h]	**1h** M_n (NMR) = 2.6 kg/mol	100	THF ($\eta = 0.4$)	97[d]	97.3[d]	1.29[d]
9[h]	**1i** M_n (NMR) = 1.9 kg/mol	50	THF ($\eta = 0.4$)	93[e]	72.4[e]	1.25[e]
10[i]	**1j**	100	None	99	26.3[d]	2.48[d]
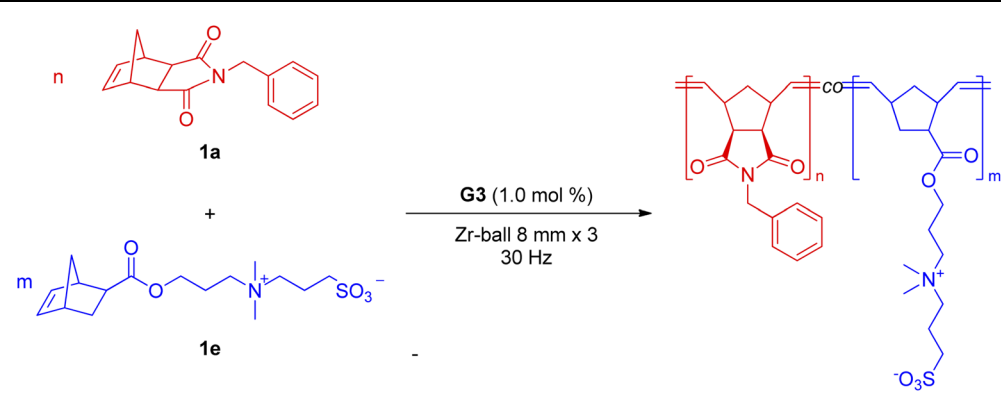
[a] Average values from two experiments. [b] Reaction conditions: monomer **1a** (50 mg), **G3**, and liquid (20 μL) in a 10 mL zirconia jar containing three zirconia balls (8 mm diameter), followed by 30 Hz vibration for 30 min. [c] Determined using ^{1}H NMR spectroscopy. Conv. (%) = a portion of polymeric alkenes of total alkenes. [d] Determined using SEC with PS standards in THF at 40 °C. [e] Determined using SEC with PS standards in DMF at 40 °C. [f] Products did not elute the column. [g] Determined using SEC with poly(ethylene oxide) (PEO) standards in H$_2$O at 40 °C. [h] Milling time = 60 min. [i] **1j** (57 μL) and **G3** in a 10 mL Teflon jar containing three zirconia balls (8 mm diameter).

Copolymers composed of neutral and ionic monomers are found in many applications.[19] However, the orthogonal solubility of monomers leads to a lack of common solvents, which has challenged their polymerization in a one-pot process. Related polymers have been prepared using multi-step polymerizations or post-polymerization modifications.[20] For the

Table 4 Copolymerizations of immiscible monomers with **G3**.[a,b]

| Entry	n : m (mol ratio)	LAG	Time (min)	Conv.[c] (1a/1e)	M_n (kg mol^{-1})	Đ	T_g (°C)
Poly-**1a**	1 : 0						116
1	10 : 1	THF (18.2 μL) + H$_2$O (1.8 μL)	30	96%/99%	14.2[d]	1.38[d]	137
2	4 : 1	THF (16 μL) + H$_2$O (4 μL)	30	99%/99%	14.0[d]	1.36[d]	143
3	2 : 1	THF (13.3 μL) + H$_2$O (6.7 μL)	30	99%/99%	15.5[d]	1.30[d]	154
4	1 : 2	THF (6.7 μL) + H$_2$O (13.3 μL)	30	99%/99%	14.2[e]	1.39[e]	153
5	1 : 4	THF (4 μL) + H$_2$O (16 μL)	30	99%/99%	17.4[e]	1.40[e]	156
6	1 : 10	THF (1.8 μL) + H$_2$O (18.2 μL)	30	99%/99%	18.1[e]	1.40[e]	161
Poly-**1e**	0 : 1						170

[a] Average values from two experiments. [b] Reaction conditions: **1a** + **1e** (50 mg), **G3** (1.0 mol%), and LAG liquid (20 μL) in a 10 mL zirconia jar containing three zirconia balls (8 mm diameter), followed by 30 Hz vibration. [c] Determined using ^{1}H NMR spectroscopy. Conv. (%) = a portion of polymeric alkenes of total alkenes. [d] Determined using SEC with PS standards in THF at 40 °C. [e] Determined using SEC with PEO standards in H$_2$O at 40 °C.

case of Ru-based ROMP, the compatibility of the Ru-initiator with monomers is also a concern. As previously stated, polymerization in a hydrophilic system necessitated Ru-initiator modification, such as adding a polar unit to a ligand.[15] However, these initiators are not compatible with hydrophobic monomers and *vice versa*. Several recent studies have shown that immiscibility in solution is not a problem under ball milling settings.[21] For example, solvent-free direct ball milling was used for post-polymerization modification of hydrophobic polymers and ionic reagents[21a] or ionic polymers and hydrophobic reagents.[21b] Bielawski also showcased the atom transfer

radical polymerization of incompatible monomers in the solid-state.[10f] Thus, we envisioned that mech-ROMP would copolymerize monomers of orthogonal solubility with one initiator. Table 3 shows that regardless of the polarity of the monomers, mechanochemical ball milling with **G3** resulted in high conversion. Subsequently, their copolymerizations were investigated. In ball milling, the hydrophobic monomer **1a** and the ionic monomer **1e** were polymerized, resulting in copolymers with varying compositions (Table 4). After each reaction, an aliquot was transferred to quantify the amount of unreacted monomers. All reactions exhibited good conversion of both **1a**
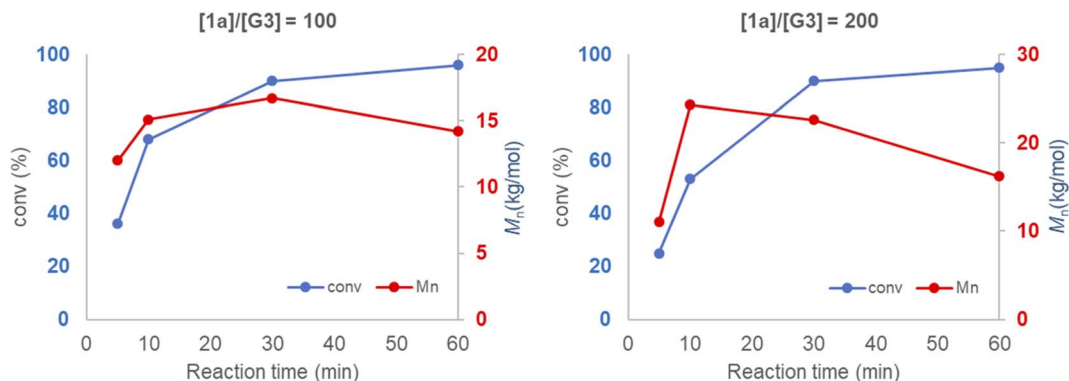
Fig. 2 Conversion and M_n vs. ball milling time of neat **1a** and **G3**.

and **1e**, and LAG was necessary for highly efficient copolymerizations.

The solubility of the resulting copolymers was dictated by the major component. Hydrophobic polymers were produced in entries 1–3, and hydrophilic polymers in entries 4–6. Only signals from the major components were observed in the ^{1}H-NMR spectra (Fig. S4 and S5†). However, the coexistence of two repeat units was established by IR spectroscopy (Fig. S3†). The peak corresponding to S=O (1034 cm^{-1}) in **1e** and the peaks corresponding to C–N (1165 cm^{-1}) and C=O (1697 cm^{-1}) in **1a** were observed for all copolymers. The measured T_g values of each copolymer also supported copolymer formation. Differential scanning calorimeter (DSC) traces exhibited a single glass transition. The T_g values changed gradually from 116 °C (poly-**1a**) to 170 °C (poly-**1e**) with increasing **1e** composition (Fig. S6†). These observations excluded the formation of mixtures of poly-**1a** and poly-**1e** or block-like structures, which would give rise to two separate glass transitions. Finally, we attempted to dissolve both monomers at various molar ratios in a large volume of THF/water mixtures (targeting [M] = 0.5 M) to pursue the possibility of solution copolymerizations (Fig. S15†). However, full monomer solubilization was not observed in any case, implying that statistical copolymerization in the solution state was not possible.
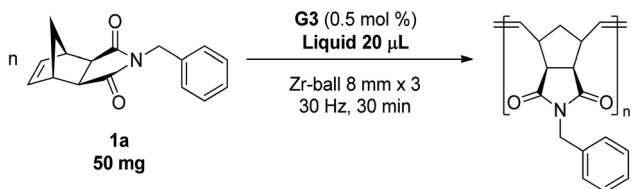
LAG: retarding mechanically induced chain-degradation

Mechanical force induces both polymerization and chain degradation.[6] To evaluate its effect on mechanochemical ROMP, the polymerization reaction of neat monomer **1a** and **G3** was monitored with increasing ball milling time (Fig. 2). The conversion and M_n were plotted *versus* the reaction time for two different initiator-to-monomer **1a** ratios ([**1a**]/[**G3**] = 100 and 200). The conversion reached >90% completion after 30 min under both polymerization reaction conditions. However, the

molecular weight growth did not follow the monomer conversion. In the case of [**1a**]/[**G3**] = 100, the highest M_n (16.7 kg mol^{-1}) was obtained at 30 min (90% conversion); further increasing the ball milling time gave a diminished molecular weight (60 min, 96% conversion, 14.2 kg mol^{-1}). When using [**1a**]/[**G3**] = 200, the final product did not exhibit a two-fold increase in the M_n when compared to the product obtained using [**1a**]/[**G3**] = 100; however, the product exhibited a similar M_n (16.2 kg mol^{-1}). Reaction monitoring revealed that the maximum M_n (24.3 kg mol^{-1}) was reached at an early stage of the polymerization (10 min, 50% conversion). Gradual degradation was observed upon the further reaction of the monomer. These results imply that chain propagation and degradation occur at the same time. The chain degradation process was considerable after $M_n \sim 15$ kg mol^{-1}. Similar observations have been repeatedly reported in the ball milling synthesis of poly(-phenylene vinylene),[9a] poly(lactic acid),[10a] poly(trimethylene carbonate),[10c] polyphenylene,[9c] and poly(2-vinyl naphthalene).[10e] To elucidate the nature of chain-degradation in Mech-ROMP, separately prepared poly-**1a** ($M_n = 33.3$ kg mol^{-1}) was ground in otherwise identical milling conditions. Fast chain-degradation to 18.2 kg mol^{-1} in 30 min suggested that mechanical force can solely cause the chain-degradation process (Table S7†). Another possibility is that the decreased molecular weight originates from the chain backbiting reaction of the reactive Ru-chain end.[22] However, the backbiting process is dominant when the monomer concentration is low. In this case, the decrease in the molecular weight begins at a low monomer conversion. Thus, mechanical action was proposed to be the dominant cause of the chain scission process.

LAG was examined to alleviate the chain degradation process (Table 5 and Fig. 3). Previously, we observed that the addition of a very small portion of liquid could reduce the chain degradation process.[10a,b] The uniform distribution of small molecules in the polymer matrix was expected to lubricate the polymer

Table 5 Effect of liquid-assisted grinding^{a,b}

Entry	Liquid	Conv.^{c} (%)	$M_n{}^d$ (kg mol^{-1})	$M_w{}^d$ (kg mol^{-1})	$M_p{}^d$ (kg mol^{-1})	Đ
1	None	90	22.6	37.7	33.7	1.67
2	Toluene	99	23.1	38.9	46.7	1.71
3	THF	96	25.7	44.6	55.7	1.74
4	DCE	99	32.3	43.4	46.1	1.35
5^e	DCE (solution)	99	40.4	48.1	51.4	1.19
6^f	DCE (20 µL) mechanical stirring	< 1	—	—	—	—

^{a} Average values from two experiments. ^{b} Reaction conditions: **1a** (50 mg), **G3**, and liquid (20 µL) in a 10 mL zirconia jar containing three zirconia balls (8 mm diameter), followed by 30 Hz vibration for 30 min. ^{c} Determined using ^{1}H NMR spectroscopy. Conv. (%) = a portion of polymeric alkenes of total alkenes. ^{d} Determined using SEC with PS standards in THF at 40 °C. ^{e} Reactions were performed using 0.4 mL of solvent ([M] = 0.5 M) for 30 min. ^{f} Reaction was proceeded in 20 µL DCE solvent in a V-shaped vial with magnetic stirring.
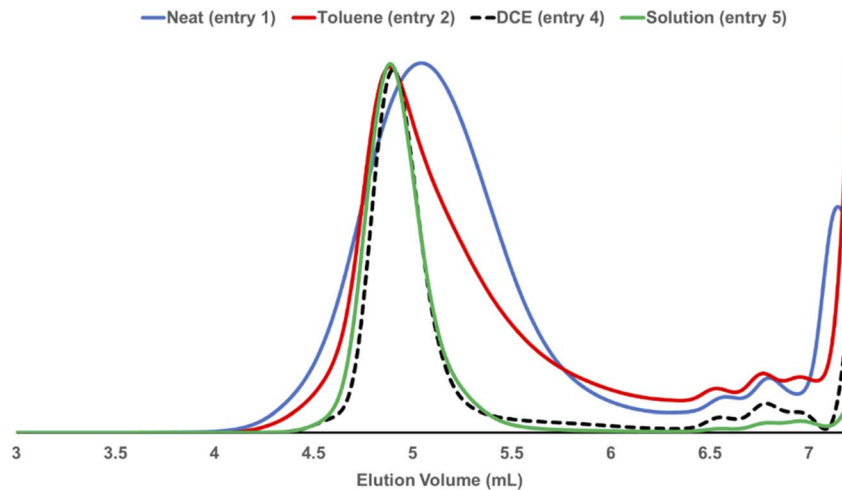
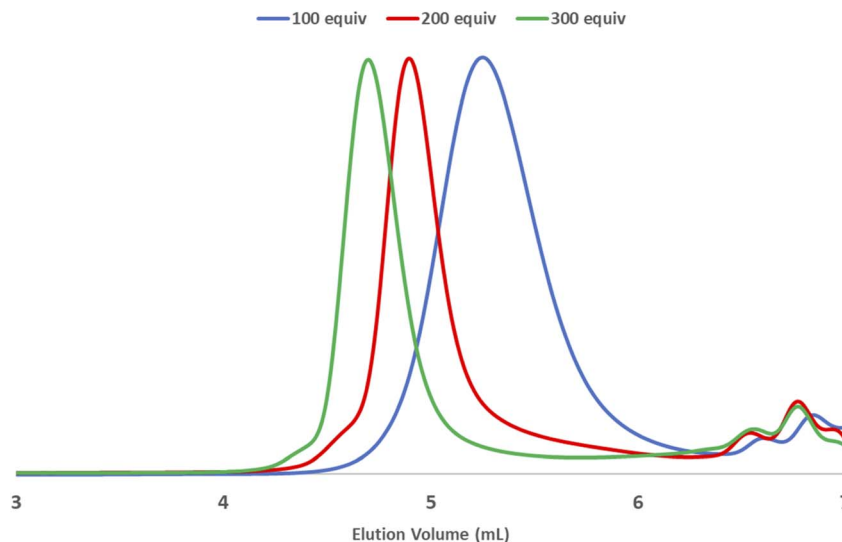Fig. 3 SEC traces obtained for selected polymers from Table 5.

Fig. 4 SEC traces of [1a]/[G3] = 100, 200, and 300. [1a (50 mg), G3, and DCE (20 μL) in a 10 mL zirconia jar, three 8 mm zirconia balls, and 30 Hz vibration for 30 min].

chains or dissipate the impact energy. Therefore, 20 μL of the selected liquid ($\eta = 0.4$ μLmg^{-1}) was added to the mixture consisting of monomer **1a** (50 mg) and **G3** (0.5 mol%). We chose a group of solvents conventionally used in Ru-ROMP for our LAG experiments (entries 2–4) and compared them with their corresponding neat grinding (entry 1) and solution-phase reactions (in DCE, entry 5). Toluene did not effectively improve the M_n (entry 2). THF resulted in a marginal increase of 3.1 kg mol^{-1} in the M_n and an improvement of 6.9 kg mol^{-1} in the M_w (entry 3). Interestingly, 1,2-dichloroethane (DCE) exhibited a substantial effect (entry 4) with an ~10 kg mol^{-1} increase in the M_n and a significant narrowing of the dispersity ($Đ = 1.35$). To gain more details on the LAG effect, we compared the shape of the SEC traces obtained for selected polymer products (Fig. 3). The addition of toluene gave similar M_n and M_w to the neat grinding reaction (entry 1, blue line in Fig. 3).

However, the peak molecular weight (M_p) of the toluene LAG polymerization product (46.6 kg mol^{-1}, red line in Fig. 3) was 12.9 kg mol^{-1} higher than that obtained using neat grinding (33.7 kg mol^{-1}, blue line in Fig. 3) and close to the M_p of the solution-phase reaction (51.4 kg mol^{-1}, green line in Fig. 3). Thus, LAG with toluene efficiently protects the polymer chains from mechanical forces. The increased small M_w portion, which was probably due to the slow initiation, accounts for the low M_n. In the case of THF (entry 3), the M_p shifts to a higher value when compared to the solution-phase reactions. Chain protection and rapid initiation were simultaneously achieved when DCE was added (dashed line in Fig. 3). It is feasible that a small amount of a liquid could promote a highly concentrated solution polymerization, with no need for milling.[23] To rule out this possibility and deduce the apparent LAG additive effect, the reaction mixture of entry 4 was placed in a V-shape vial, and

magnetic stirring was applied (Fig. S17†). After 30 min, no polymer was detected by ^{1}H-NMR. Therefore, mechanochemical ball-milling was necessary to promote the polymerization, and LAG helped both material dispersion and chain protection. The use of LAG also enabled the synthesis of high-molecular-weight polymers. A gradual increase in the molecular weight of poly-**1a** was observed with increasing [**1a**]/[**G3**] using **G3** and DCE (20 μL) (Table S9† and Fig. 4). At [**1a**]/[**G3**] = 100, 200 and 300, polymers with $M_n = 15.2 \pm 0.9$ kg mol^{-1} ($Đ = 1.54 \pm 0.01$), $M_n = 31.7 \pm 1.8$ kg mol^{-1} ($Đ = 1.43 \pm 0.11$) and $M_n = 53.1 \pm 2.1$ kg mol^{-1} ($Đ = 1.13 \pm 0.04$) were obtained.

Conclusion

We have shown that ROMP, one of the most versatile methods used for functional polymer synthesis, is possible under mechanochemical ball milling conditions. Unmodified Ru-alkylidene **G3** maintained its reactivity and versatility in the solid state, and the mechanical energy clearly regulated the mech-ROMP process, likely following a similar mechanism to the solution-based ROMP. The mech-ROMP examples showcased enhanced green chemistry and broadening of the field. Efficient mixing and energy supply by ball milling significantly lowered the solvent portion. The polymerization of immiscible reagents such as hydrophilic and hydrophobic monomers produced mechano-exclusive polymers, which will lead the expedition to new properties and applications.

Experimental

General experimental procedure for mech-ROMP (Table 5, entry 4)

All chemical transfers and vessel assemblies were conducted in a nitrogen-purged dry-box. Monomer **1a** (50 mg) and DCE (20 μL) were added to a zirconia milling container (10 mL) having 8 mm zirconia balls (3 ea.). A solution of **G3** in DCE was added to the top closure. This part was left for a minute to allow the DCE to evaporate, leaving the designated amount of **G3** (0.50 mol%). The main vessel and top closure were assembled. The vessel was placed in a vibrational ball milling machine and milled for 30 min in a thermostat at 30 °C. The milling vial was opened. A few drops of ethyl vinyl ether were added to quench the polymerization, followed by an additional 5 min of ball milling. A portion of the solid mixture was subjected to ^{1}H NMR spectroscopy and SEC analysis to determine the conversion and molecular weights. The average of the two experiments was reported: 99% conversion (^{1}H NMR, CDCl$_3$); $M_n = 32.3$ kg mol^{-1}, and $Đ = 1.29$ (SEC in THF, PS-standard).

Data availability

All experimental data and detailed experimental procedures are available in the ESI.†

Author contributions

J. G. K. and T. F. conceived, designed, and initiated this project. D. T. conducted the initial experiments. G. S. L, H. W. L, H. S. L, and J.-L. D. performed the experiments, obtained all data and analysed the results. J. G. K. and G. I. P. validated all data. J. L. provided the fluorine monomer and confirmed the data. J. G. K. wrote the original draft, and G. I. P. reviewed and edited the manuscript. All authors read and confirmed the manuscript and ESI.†

Conflicts of interest

The authors declare no competing financial interest.

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