Mechanochemical Ring-Opening Metathesis Polymerization: Development, Scope, and Mechano-Only Copolymer Synthesis

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Abstract

Ruthenium-alkylidene initiated ring-opening metathesis polymerization (Ru-ROMP) was realized under solid-state conditions employing a mechanochemical ball milling method, promoting greenness and broadening scope. High-speed ball milling provided sufficient mixing and energy to the reaction mixture comprised of the catalyst and solid monomers, thus eliminating the need for solvents. Studies on the catalytic species and ball milling parameters (liquid-assisted grinding, vibration frequency, and ball size) revealed that mechanical energy regulated solid-state Ru-ROMP and it follows similar mechanistic features of solution-phase reactions. The solubility and miscibility of monomer and Ru-initiator are not a limitation in solid-state ball milling. Without the use of a solvent, a wide spectrum of solid monomers, including ionomer, fluorous monomer, and macromonomers, were successfully polymerized. Finally, effective direct copolymerization of immiscible monomers such ionic/hydrophobic and ionic/fluorous monomers resulted

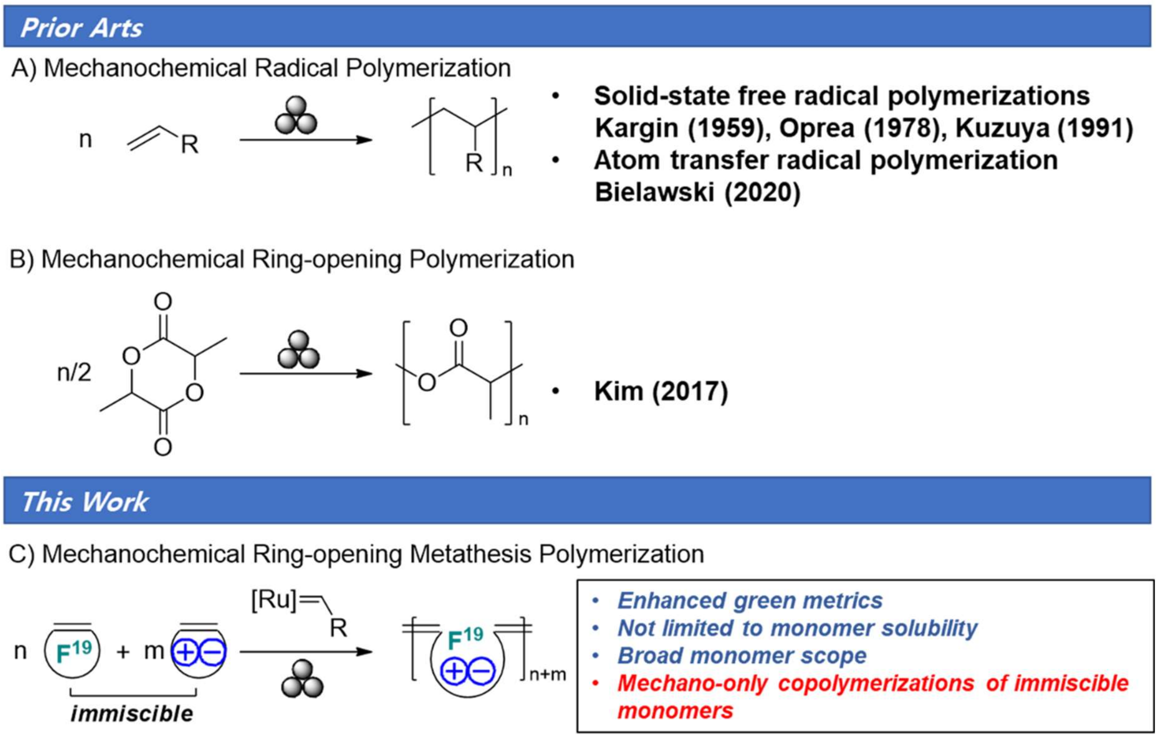
in a set of copolymers that are difficult to make using traditional solution procedures.

Introduction

Mechanochemical synthesis is a chemical transformation induced by mechanical forces.[1] Efficient mixing and energy delivery using mechanical methods, such as ball milling, have many merits such as solvent-free green synthesis conditions, enhanced reactivity, and unexpected selectivity that conventional methods do not have.[2] Over the years, mechanochemical syntheses have been successfully established in many areas along with a better understanding of mechanical actions.[3]

For a long time, mechanochemistry has been considered by polymer chemists to be the study of the events related to chain scission or degradation.[4] Breakage and rearrangement of polymer chains induced by mechanical forces have been utilized in many applications. Mechanochemical polymer synthesis beginning with monomers also has a long history. A number of studies on solvent-free mechanochemical polymerization have been sporadically reported since the first report of ball milling free radical polymerization by Kargin in 1959 as efforts toward green and more efficient synthesis,[5] but the important studies by Oprea in the 1970s[6] and Kuzuya[7] in the 1990s have not received the attention they deserve. Green chemistry has become a significant topic and mechanochemical polymer synthesis has recently received an increasing amount of research attention.[8] In 2014, Swager demonstrated that the solid-state Gilch polymerization of 2-methoxy-5-2’-ethylhexyloxy phenylene vinylene was achieved after just 5 min of ball milling.[9] Highly efficient and reproducible polymer formation was achieved without the use of liquid-phase reagents. The Borchardt group reported the synthesis of polymers with low solubility, such as poly(phenylene) and poly(azomethine) with a high degree of polymerization.[10] Song and co-workers have demonstrated the high efficiency and promising practicality of ball milling polymerization toward the synthesis of bio-based polyurethane.[11] In addition to the aforementioned stepwise polymerization reactions, chain polymerizations have also been realized under ball milling conditions, aiming at controlled polymerization and the production of high-molecular weight products. Adding to early examples of free radical polymerizations by Kargin, Oprea, and Kuzuya (Scheme 1A),[5-7] Kim group reported the solid-state organocatalytic ring-opening polymerization of lactide and trimethylene carbonate under solvent-free ball milling conditions (Scheme 1B).[12] Chain-growth polymerizations involving three components (monomer, initiator, and catalyst) were achieved with high efficiency without the need of a solvent. Undesired chain degradation was controlled using liquid-assisted grinding, allowing a high degree of polymerization and control over the molecular weight of the polymer products.[12a,b] Recently, the controlled polymerization of a solid vinyl monomer has been reported, which can substantially expand the scope of mechanochemical polymerization.[13] Bielawski and Cho have presented the solid-state atom transfer radical polymerization of 2-vinyl naphthalene and its copolymerization with a conventionally incompatible ionomer, sodium styrene sulfonate. Chemical modification of solid polymers is possible without the need for a solvent. Several examples by Kim, Friščić, Moores, and Hobbs have proven that ball milling can efficiently promote the chemical transformation of polymeric materials and small molecules, sometimes better than their corresponding solution-phase reactions.[14] However, research on mechanochemical polymer synthesis is still in its infancy when compared to that on solution-phase polymerization. The scope of the reported examples is limited. The feasibility of many common polymerization techniques under mechanochemical conditions is obscure. Thus, the synthesis of polymers only obtainable by mechanochemical means remained unexplored.

Many examples of mechanochemical methods have been proven to provide excellent mixing and energy delivery to solid-state materials, which are comparable to their homogeneous liquid-state reactions. Sometimes, the complete dispersion of precursors that would be very difficult to achieve in the liquid state is possible by mechanochemical methods.[15] From this point of view, we envisaged that the solid-state mechanochemistry of widely applicable polymerization techniques, such as ring-opening metathesis polymerization (ROMP), will not only promote green chemistry, but also allow to polymerize previously inaccessible monomers or their combinations to form new materials. Herein, we report the development and scope, including copolymerizations previously inaccessible monomer set of ball milling-mediated ROMP in this article (Scheme 1C).



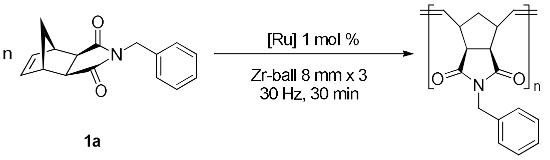
Scheme 1. Solid-state mechanochemical chain polymerizations: A) radical, b) ring-opening, and C) ring-opening metathesis polymerizations.

ROMP has deeply impacted many areas of polymer chemistry.[16] Highly active, easy to conduct, and functional group-tolerant Ru-ROMP has dramatically expanded its boundaries. A tremendous amount of effort to improve the efficiency, selectivity, and applicability of this process has been exerted; the development of a sustainable ROMP process has also attracted significant attention to maximize its economic impact and greenness.[17] Given that the solvent takes the largest volume in chemical synthesis, its impact in terms of green chemistry is the first factor to consider.[18] Less-toxic solvents or solvent-free conditions in olefin metathesis have been eagerly pursued.[19] However, only a few studies on solvent-free metathesis polymerization reactions have been reported to date. The Lalabi and Taoufik group has demonstrated the ROMP of norbornene over solid-supported tungsten-oxo catalysts.[20] The reaction was conducted in molten norbornene. However, a large amount of norbornene was left. Solvent-free Ru-ROMP has been evaluated by the Hobbs group.[21] High reactivity was observed under highly concentrated conditions, but all of the examples required a homogeneous liquid state to ensure high turnover. Meier and co-workers have demonstrated a highly efficient solvent-free acyclic diene metathesis (ADMET) polymerization reaction using a ruthenium carbene catalyst.[22] However, these systems did not include solid monomers and control over the polymerization reaction is easily lost when the mixture becomes highly viscous or solidifies. In addition, the ROMP of poorly soluble monomers has not been studied. For example, (co)polymerization of ionic monomers lacks common solvents with conventional initiator and monomers, where excellent and unique miscibility by mechanical ball-milling could provide a solution. The modification of metathesis catalysts would be avoided by direct mixing with immiscible monomers.

Results and Discussion

Rh-Initiator Screening: Ball-Milling vs Solution. Mechanochemical ruthenium-catalyzed olefin metathesis has been previously investigated by Friščić and co-workers using ring-closing and cross-metathesis reactions.[23] Solid-state metathesis is feasible without losing the reactivity. To test its applicability in polymerization, a series of representative ruthenium-alkylidene initiators were chosen to conduct ROMP including Ru-phosphine (**G1**) and highly reactive Ru-N-heterocyclic carbene (NHC) complexes (**G2**, **G3**, and **HG2**) (Scheme 2). Each initiator (1 mol%) polymerized the model norbornene monomer (**1a**) under solvent-free ball-milling conditions (Table 1). All reactions were quenched using a few drops of ethyl vinyl ether after a given vibration time.

Table 1. Scope of the initiator used in ball-milling ROMP.[a]



Entry	[Ru]	Conv[b] (%)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	*Đ*	*E*/*Z*[b]
1	G1	29	6.4	8.2	1.29	76/24
2	G2	92	14.1	23.7	1.69	57/43
3	G3	97	14.5	22.2	1.53	57/43
4	HG	98	21.3	45.1	2.12	57/43
5	G3(THF)	99	17.2	19.7	1.14	51/49

[a] 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. [b] Determined using ^{1}H NMR spectroscopy. [c] Determined using size exclusion chromatography (SEC) with polystyrene (PS) standards in tetrahydrofuran (THF) at 40 °C.

The general reactivity trends observed in the solution-phase polymerization reaction were maintained in the solid-state ball-milling ROMP.[24] Phosphine-based catalyst **G1** exhibited the slowest rate (29%) after 30 min (entry 1). **G1** was inactive in the cross-metathesis reaction in Friščić's experiments, which is not the case for ROMP.[23] Highly reactive Ru-NHC species exhibit > 90% conversion as expected (entries 2–4). Among the Ru-NHC carbene catalysts studied, **G3** with loosely coordinated and, thus, fast-initiating pyridine ligands showed the narrowest dispersity (*Đ* = 1.53, entry 2). **G2** (entry 3) and **HG2** (entry 4) bearing strong ligands result in broader molecular weight distributions, which are similar to those observed in solution-phase ROMPs. However, the dispersity of **G3** in the solid-state was still much larger than that observed in its solution-phase reaction (*Đ* = 1.14, entry 5). To obtain a narrow dispersity, the initiation rate should be higher than the propagation rate. The initiation step in ball milling involves simultaneous physical mixing, which causes a delay in the reaction of the Ru-alkylidene and the first monomer. Thus, the difference between the initiation and propagation rates can be reduced or even reversed, leading to broad dispersity. This hypothesis was supported by entry 1. The use of the slow-propagating G1 catalyst can alleviate the effect of slow and uneven initiation effects, resulting in a narrower dispersity (*Đ* = 1.29, entry 1). A similar trend in the molecular weight distribution has been previously observed in the solid-state polymerization of trimethylene carbonate using organocatalysts such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene. (TBD).[12c] The faster propagation TBD catalyst exhibits broader dispersity than the slower catalyst DBU in the ball-milling chain polymerization reaction because of the inherently retarded initiation step.

The *trans* and *cis* ratios of the product polymers were comparable to those observed in their corresponding solution-phase polymerization reactions.[25] Ru-phosphine **G1** preferably produces the (*E*)-isomer (entry 1), and the Ru-NHC catalysts (**G2**, **G3**, **HG2**) exhibited near-equivalent *E*/*Z* selectivity (entries 2–4, *E*/*Z* = 57/43). The collective results support the fact that the solid-state Ru-ROMP proceeds via a mechanism similar to that observed in the solution-phase reaction. 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 was the initial reaction temperature. At the end of the reaction, the temperature of the reaction mixture was measured using an IR thermometer (45–50 °C); this temperature was much lower than the melting point of monomer **1a** (104 °C) and the glass transition of its resulting polymer (141 °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.

Liquid-Assisted Grinding(LAG): Retarding Mechanically Induced Chain-Degradation. The polymerization reaction was monitored with the ball-milling time (Figure 1). The conversion and number-average molecular weight (M_n) were plotted versus the reaction time for two different initiator-to-monomer ratios ([**M**]/[**G3**] = 100 and 200). The conversion reached >90% completion after 30 min under both polymerization reactions. However, the molecular weight growth did not follow the monomer conversion. In the case of the [**M**]/[**G3**] = 100 reaction, the highest M_n (16.7 kg/mol) was obtained at 30 min (90%); further increasing the ball-milling time gave a diminished molecular weight (60 min, 96%, 14.2 kg/mol). When using 200 equiv. of monomer with respect to **G3**, the final product did not exhibit a two-fold increase in the M_n when compared to the product obtained using 100 equiv.; however, the product was formed with a similar M_n (16.2 kg/mol). Reaction monitoring revealed that the maximum M_n (24.3 kg/mol) was reached at an early stage of the polymerization (10 min, 50% conversion, 24.3 g/mol). Gradual degradation was observed upon 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 ~15 kg/mol. Similar observations have been repeatedly reported in the ball-milling synthesis of poly(phenylene vinylene), poly(lactic acid), poly(trimethylene carbonate), polyphenylene, and poly(2-vinyl naphthalene).[7a, 9,10,12,13] Another possibility is that the decreased molecular weight originates from the chain backbiting reaction of the reactive Ru-chain end.[26] However, the backbiting process is usually 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.

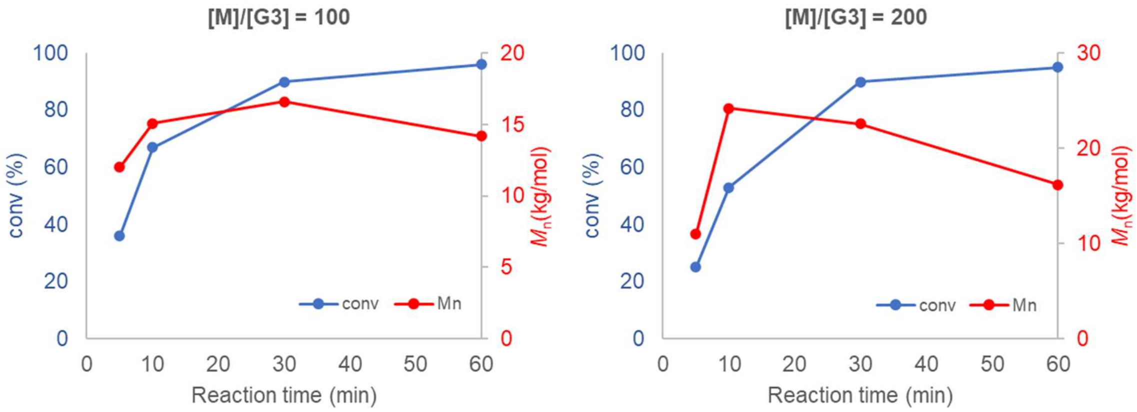
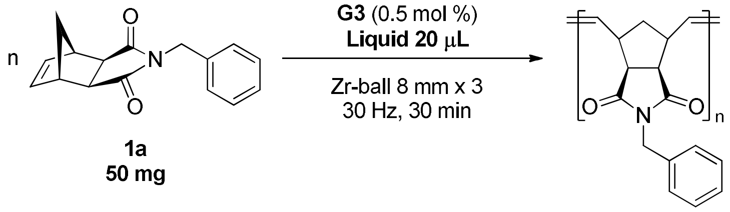


Figure 1. Conversion and number average molecular weight vs. ball-milling time.

Liquid-assisted grinding (LAG) was examined to alleviate the chain degradation process (Table 2).[27] Previously, we observed that the addition of a very small portion of liquid could reduce the chain degradation process.[12a,b] The uniform distribution of small molecules in the polymer matrix was expected to lubricate the polymer chains or dissipate the impact energy. Therefore, 20 μL of the selected liquid (η = 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 (entries 5 and 6). Toluene did not effectively improve the M_n (entry 2). THF resulted in a marginal increase of 2.9 kg/mol in the M_n and an improvement of 6.9 kg/mol in the M_w (entry 3). Interestingly, 1,2-dichloroethane (DCE) exhibits a substantial effect (entry 4) with an ~10 kg/mol increase in the M_n and a significant narrowing of the dispersity. To gain more details on the LAG effect, we compared the shape of the gel permeation chromatograms obtained for selected polymer products (Figure 2). The addition of toluene gives similar M_n and M_w to the neat grinding reaction (entry 1, blue line in Figure 2). However, the peak molecular weight (M_p) of the toluene added polymerization product (46.6 kg/mol, red line in Figure 2) was 12.9 kg/mol higher than that obtained using neat grinding (33.7 kg/mol) and nearly identical to the M_p of the solution-phase reaction (48.0 kg/mol, green line in Figure 2). 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 fast initiation were simultaneously achieved when DCE was added (dashed line in Figure 2). LAG helped both material dispersion and chain protection.

Table 2. Effect of liquid-assisted grinding.[a]



Entry	Liquid	Conv[b] (%)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	M_p[c] (kg/mol)	$Đ$
1	None	89	22.6	37.7	33.7	1.67
2	Toluene	99	23.0	38.9	46.6	1.71
3	THF	96	25.5	44.6	55.7	1.74
4	DCE	99	32.3	43.4	46.1	1.29
5[d]	THF (Solution)	99	40.0	46.5	48.0	1.16
6[d]	DCE (Solution)	99	40.4	48.1	51.4	1.19

[a] 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. [b] Determined using ^{1}H NMR spectroscopy. [c] Determined using SEC with PS standards in THF at 40 °C. [d] Reactions were performed using 0.4 mL of solvent ([M] = 0.5 M) for 30 min.

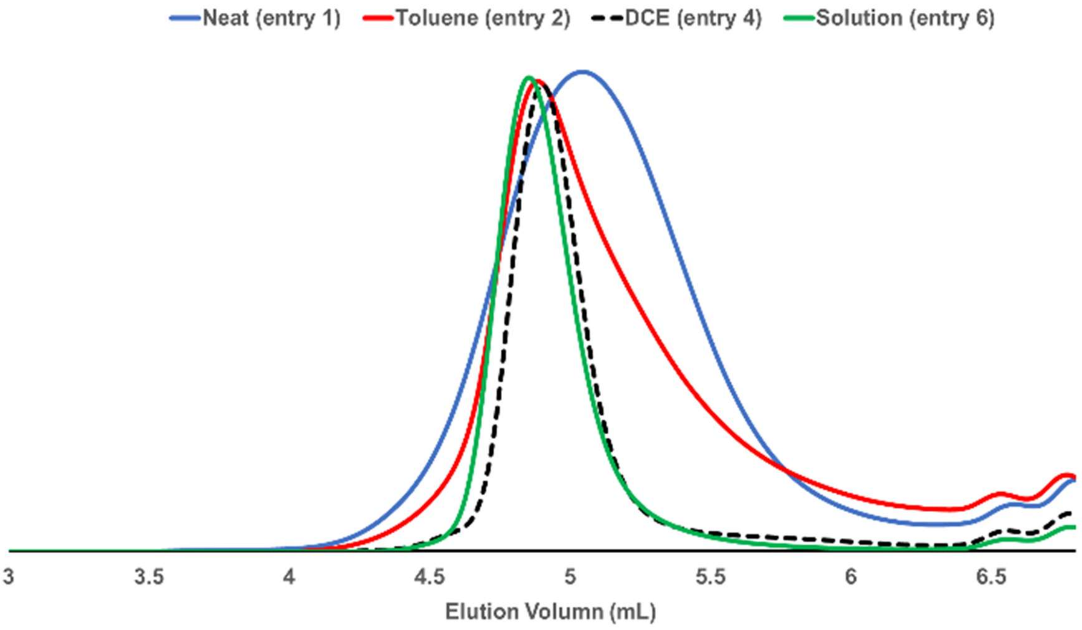
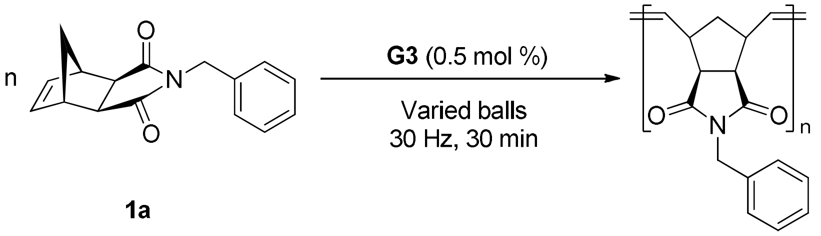


Figure 2. SEC traces obtained for selected polymers from Table 2.

Evaluation of Ball-Milling Parameters. Subsequently, different milling parameters were investigated (Table 3). To evaluate both the polymerization and degradation efficiency, [**M**]/[**G3**] = 200 was used. Changing the number of milling balls was not an important 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). The degradation levels were similar. Similar molecular weights were obtained regardless of the number of milling balls used. However, variations in the ball size had a pronounced effect on the polymerization reaction. Changing to a heavier 10 mm ball resulted in the full consumption of the monomer, whereas the use of 5 mm balls (× 12) only gave a 16% turnover and 3 mm balls (× 20) showed almost no conversion. As seen in ring-opening lactide polymerization,[12a] the importance of the collision energy on the reaction efficiency was again confirmed in ROMP. At the same time, high-energy ball milling affected the degree of chain degradation. The experiment using a 10 mm ball produced a polymer product with a lower number average molecular weight than that obtained using 8 mm ball conditions (24.1 vs. 16.5 kg/mol). The effect of the vibration frequency was evaluated at 20 Hz (entry 7). Slower vibration provided poor mixing and low-energy delivery, resulting in a low conversion (16%).

Table 3. Effect of the ball-milling parameters.[a]



Entry	Balls	Conv[b] (%)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	*Đ*
1	8 mm × 1	87	24.1	39.5	1.64
2	8 mm × 3	90	22.6	37.7	1.67
3	8 mm × 5	93	23.0	37.8	1.65
4	10 mm × 1	98	16.5	27.2	1.65
5	5 mm × 12	16	N/A	N/A	N/A
6	3 mm × 20	1	N/A	N/A	N/A
7	8 mm × 3 (20 Hz)	16	N/A	N/A	N/A

[a] Reaction conditions: **1a** (50 mg) and **G3** in a 10 mL zirconia jar, followed by 30 Hz vibration for 30 min. [b] Determined using ^{1}H NMR spectroscopy. [c] Determined using SEC with PS standards in THF at 40 °C.

Livingness & Block Copolymerization. One of the most important features of Ru-ROMP is its livingness. The active chain end after full consumption of the monomer can accept a second monomer, resulting in its corresponding block copolymer. To evaluate livingness, the sequential addition of **1a** was investigated. After 10 min of grinding of the first portion of monomer **1a** (100 equiv., 91% conversion) and **G3**, the second portion of **1a** (100 equiv.) was added, and grinding continued. However, a large portion of the first block remained unreacted (Figure 3). Therefore, the formation of block copolymers via the sequential addition of the monomer was not viable. As of now, it is not clear what occurs at the ruthenium alkylidene end; further studies, including the termination pathway under solid-state conditions, are ongoing in our laboratory.

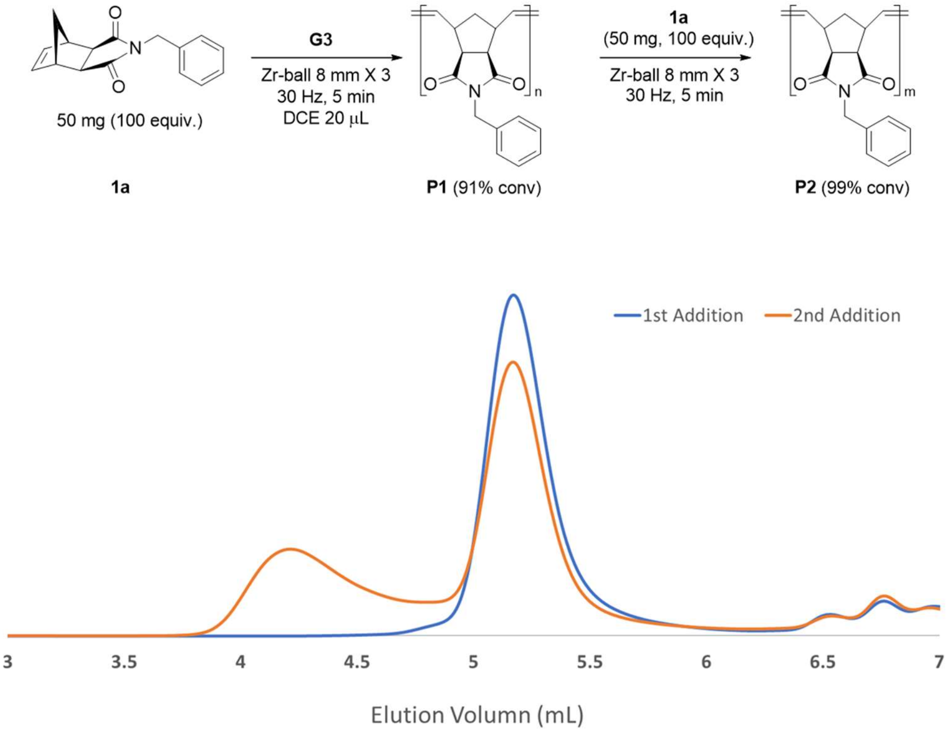
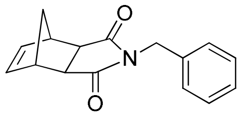
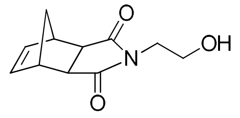
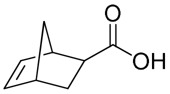
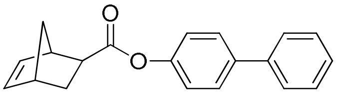
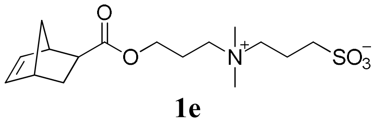
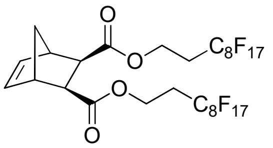
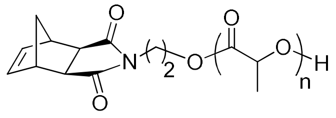
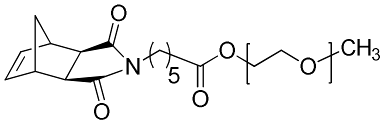


Figure 3. SEC traces obtained of sequential monomer **1a** addition experiment.

Scope of Monomers. A variety of solid monomers were used under the optimized ball-milling polymerization conditions (Table 4). 100 to 300 equiv. of monomer **1a** were polymerized and a linear increase in the molecular weights was observed (entries 1–3). The LAG of DCE ($\eta = 0.4$) minimized chain degradations: a control of molecular weight was achieved. The high functional group compatibility of the ruthenium metathesis catalyst was also observed in the solid-state ROMP. Initiator **G3** maintained its metathesis reactivity in the presence of highly concentrated hydroxy (**1b**), carboxylic acid (**1c**), and ester (**1d**) groups (entries 4–6). Exceptional mixing efficiency of high-speed ball milling has great potential in polymerization of monomers with orthogonal solubilities to **G3**. Several Ru-ROMP examples in aqueous media have been previously reported.[28] However, modification of the Ru catalyst with ionic pendants was required to make the catalyst soluble in water. In the solid-state ball milling ROMP, the unmodified **G3** initiator exhibits excellent efficiency (99%) in the polymerization of zwitterionic monomer **1e** (entry 7). Next, the production of a fluorous polymer was achieved by direct ball milling. The highly fluorine-enriched monomer **1f** was commenced to G3 initiator (entry 8). The LAG of a 1:1 mixture of THF and HFE-7100 ($C_4F_7OCH_3$) ($\eta = 0.4$) provided sufficient mixing of **1f** and **G3**, and the corresponding fluorous-polymer was obtained quantitatively. Another interesting class of monomers, norbornenyl-terminated macromolecules (NB-MM), can be polymerized (entries 9 and 10), giving bottlebrush polymers.[29] 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) and poly(ethylene glycol) macromonomers were efficiently polymerized using THF-LAG.

Table 4. Scope of the monomer in the solid-state ROMP.[a]

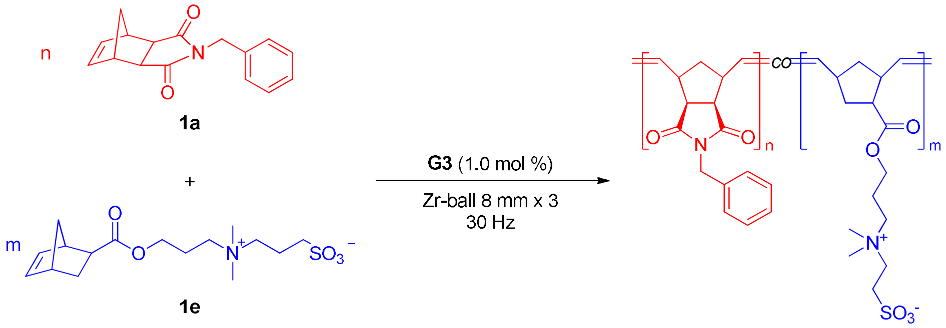
Entry	Monomer	[M]/[G3]	LAG	Conv[b] (%)	M_n[c] (kg/mol)	$Đ$
1	 **1a**	100	none	97	14.5	1.53
2		200	DCE (η = 0.4)	99	32.3	1.29
3		300	DCE (η = 0.4)	99	54.9	1.17
4	 **1b**	100	none	98	69.9[d]	1.72[d]
5	 **1c**	100	none	97	N/A	N/A
6	 **1d**	100	none	91	18.2	1.53
7	 **1e**	100	H_2O (η = 0.4)	99	24.7[e]	1.36[e]
8	 **1f**	50	THF/HFE [d] (1:1) (η = 0.4)	99	N/A	N/A
9[f]	 M_n (NMR) = 2.6 kg/mol **1g**	100	THF (η = 0.4)	96	97.3	1.29
10[f]	 M_n (NMR) = 1.9 kg/mol **1h**	50	THF (η = 0.4)	93	72.4[d]	1.25

[a] 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. [b] Determined using ^{1}H NMR spectroscopy. [c] Determined using SEC with polystyrene standards in tetrahydrofuran at 40 °C. [d] Determined using SEC with polystyrene standards in dimethylformamide at 40 °C. [e] Determined using SEC with poly(ethylene oxide) standards in H_2O at 40 °C. [f] Milling time = 60 min.

Synthesis of Mechano-only Copolymers. Copolymers comprised of neutral and ionic monomers are found in many applications.[30] However, the orthogonal solubility of these monomers, thus lack of common solvents, has challenged their synthesis. Multi-step polymerization and post-polymerization modifications have been practiced.[31] The compatibility of Ru-initiator with monomers is also a concern in the Ru-ROMP.[28] As previously stated, polymerization in a hydrophilic system necessitated Ru-complex modification, such as the addition of a polar unit to a ligand. However, those initiators are not compatible with hydrophobic monomers and vice versa. Several recent studies have shown that under ball milling settings, immiscibility in solution is not a problem. Solvent-free direct ball milling was used to successfully combine a hydrophobic polymer and ionic reagents[14a] or an ionic polymer and hydrophobic reagents.[32] Bielawski also showcased the ATRP of incompatible monomers in solid-state.[13] Thus, we envisioned that mechanochemical ROMP would copolymerize monomers of orthogonal solubility with one initiator. Table 4 shows that regardless of the polarity of the monomers, including ionic and fluorous monomers, mechanochemical ball-milling with **G3** produced high polymerization efficiency. 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 5). After each reaction, an aliquot was transferred to trace unreacted monomers. Most of the reactions exhibited good concurrent conversion of both **1a** and **1e** except entry 4 that the minor component hydrophobic **1a** reached 83% conversion while hydrophilic **1e** was consumed completely. The solubility of the resulting copolymers was dictated by the major component. Hydrophobic polymers were produced in entries 2 and 3, and entries 4 and 5 were hydrophilic polymers. Only main components were found using ^{1}H-NMR spectrometers (figure S3). The coexistence of two repeat units was established by the IR spectra (figure S4). The peak of S=O

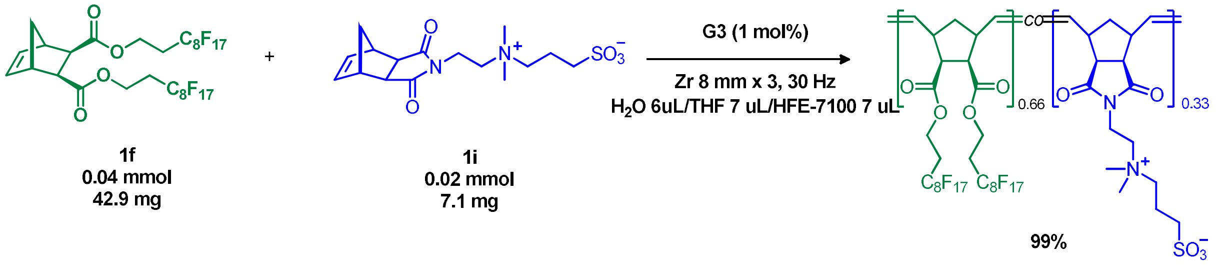
(1034 cm^{-1}) in **1e** coexisted with the peaks of C-N (1165 cm^{-1}) and phthalimide (1717 cm^{-1}) in **1a** in all copolymers. The copolymerization of fluorous (**1f**) and ionic (**1i**) monomers took place under similar conditions (Scheme 2). ROMP of **1f** and **1i** (1:2 ratio) gave the corresponding copolymer. The product's IR spectra revealed both peaks, **1f** ester and **1i** phthalimide (figure S5). The relative intensities of the peaks matched those of the monomer mixture, proving successful copolymerization that is hard to obtain in solution conditions.

Table 5. Copolymerizations of immiscible monomers with **G3**.



Entry	n : m	LAG	Time (min)	Conv[b] (**1a**/**1e**)	M_n[c] (kg/mol)	M_w[c] (kg/mol)	*Đ*
1	1:0	THF (20 μL)	30	94%/--	15.2	20.1	1.32
2	10:1	THF (20 μL)	60	91%/99%	12.5	16.9	1.36
3	4:1	THF (16 μL) + H_2O (4 μL)	60	98%/99%	16.6	20.8	1.25
4	1:4	THF (4 μL) + H_2O (16 μL)	30	83%/99%	29.0	36.6	1.26
5	1:10	H_2O (20 μL)	30	99%/99%	24.8	30.7	1.24
6	0:1	H_2O (20 μL)	30	--/99%	24.7	33.5	1.36

[a] Reaction conditions: **1a** + **1e** (50 mg), **G3** (1.0 mol%), and liquid (20 μL) in a 10 mL zirconia jar containing three zirconia balls (8 mm diameter), followed by 30 Hz vibration. [b] Determined using ^{1}H NMR spectroscopy. [c] Determined using SEC with polystyrene standards in tetrahydrofuran at 40 °C. [d] Determined using SEC with polystyrene standards in dimethylformamide at 40 °C. [e] Determined using SEC with poly(ethylene oxide) standards in H_2O at 40 °C.



Scheme 2. Copolymerization of immiscible fluorous monomer (**1f**) and ionomer (**1i**).

Conclusion

We have proven that ROMP, one of the most versatile methods used for functional polymer synthesis, is possible under solid-state ball milling conditions. Unmodified Ru-alkylidene **G3** maintained its reactivity and versatility without the need for a solvent. High-speed ball milling provides sufficient mixing and energy. The use of liquid additives has a positive effect. LAG is essential for the preparation of polymer products with high molecular weight and narrow dispersity. This mechanochemical system showed a broad monomer scope, including challenging classes such as ionic and fluorous monomers as well as macromonomers. The orthogonal solubilities among monomers and initiators were not a problem anymore in solid-state ball milling conditions. The copolymerization examples of hydrophobic/ionic monomers and fluorous/ionic monomers produced mechano-only polymers, which allowed the expedition to new properties and applications, which will follow by our further research.

Methods

General experimental procedure for ball milling-promoted ROMP (Table 2, entry 4).

All chemical transfers and vessel assembly were conducted in a nitrogen-purged dry-box. Monomer **1a** (0.20 g) and DCE (40 mL) 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, $Đ$ = 1.29 (SEC in THF, PS-standard).

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Author information

Contributions

J.G.K. and T.F. conceived, designed, and originated 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 date and analysed the results. J.G.K and T.F. wrote the manuscript. J.L. provided fluorine monomer and confirmed the data. All authors read and confirmed the manuscript and supporting information.

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