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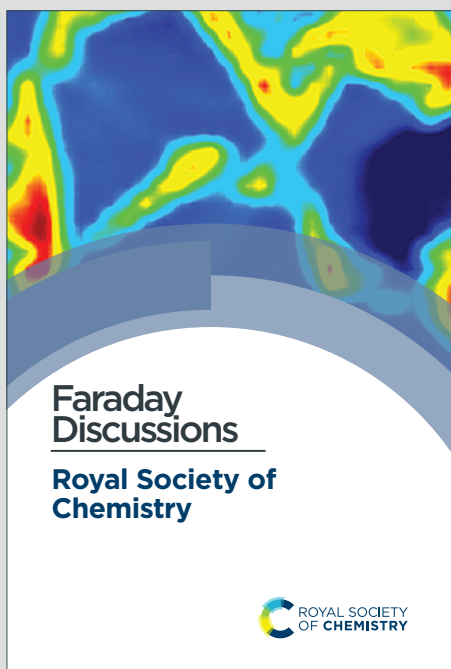OF CHEMISTRY

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ARTICLE

Mechanochemical Solid-State Vinyl Polymerization with Anionic Initiator

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Mechanochemistry has been extended to various polymer syntheses to achieve efficiency, greenness, and new products. However, many fundamental polymerization reactions have not been explored, although anionic polymerization of vinyl compounds has been pursued under mechanochemical conditions. Two solid monomers, 4-biphenyl methacrylate and 4-vinyl biphenyl, each representing methacrylate and styrenic classes, respectively, were reacted with secondary butyl lithium under high-speed ball-milling. The alkyl-anion-promoted polymerization process was established by excluding radical initiation and producing the expected polymers with good efficiency. However, the generally expected features of anionic polymerization, such as molecular weight control and narrow dispersity, were not observed. Analysis of the milling parameters, reaction monitoring, and microstructural analysis revealed that the mechanism of the mechanochemical process differs from that of conventional anionic polymerizations. The mechanical force fractured the newly formed polymer chains via anionic initiation and generated macroradicals, which participated in the polymerization process. The anionic process governs the initiation step and the radical process becomes dominant during the propagation step.

Introduction

Mechanochemistry has become a significant choice in synthetic chemistry. Mechanical motions such as collision and friction in ball-milling or shearing in twin-screws allow direct mixing of reagents and supply energy. Reducing or eliminating the solvent in the mechanochemical process results in cleaner, faster, and more straightforward synthesis than in conventional systems.[1] Mechanochemistry also provides a resolution to the issue of differences in the solubility of the reagents or the decomposition of intermediates in solution.[2] This process can also produce new compounds that are inaccessible in solution. Almost all areas of synthetic chemistry have examples that demonstrate the virtue of mechanochemistry.[3]

These advantages have also affected the polymer synthesis community. Historically, the mechanochemistry of polymers has meant the involvement of chain degradation, molecular weight reduction, and mechanical deterioration.[4] The construction of macromolecular structures from small molecules using mechanical forces has evolved.[5] Since Kargin's pioneering works on the polymerization of styrenic and acrylic monomers in the 1950s, there have been some sporadic reports that mostly focused on radical polymerization.[6] In the 21st century, which is the era of green chemistry, attention to mechanochemical polymer synthesis has increased. Various polymerization techniques are now on the list of mechanochemistry, such as radical polymerization of vinyl compounds,[6] ring-opening polymerization of cyclic esters and carbonates,[7] metathesis polymerization,[8] and step polymerization to generate polyaniline, polyphenylene, poly(phenylene vinylene), and polyurethane.[9] These examples demonstrate that mechanochemical polymer synthesis offers many merits such as a) advancing green metrics in polymer science, b) improving the efficiency of syntheses, c) better performance of the resulting polymers, and d) polymerization of monomers or producing polymers with limited solubility.

However, many polymerization methods, including anionic polymerization, have not been validated under mechanochemical conditions. Fast initiation and propagation by highly nucleophilic anions produce many polymeric materials in the course of daily life.[10] The high level of precision is another merit of anionic polymerization. However, reactions involving highly reactive alkyl anions require low-temperature conditions and careful handling of reagents to achieve the expected goals, which retard investigations of these reactions under other conditions.[11] With an interest in expanding the scope of mechanochemical chain polymerization,[7] our research group has commenced studies on solid-state mechanochemical polymerization of an anionic

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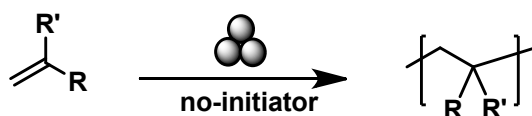† These authors contributed equally

initiator and vinyl monomers and found distinctive characteristics compared to the solution systems. Anionic initiators promote the initiation step, but propagation is a radical process. The details of our study and its findings are presented herein (Figure 1).
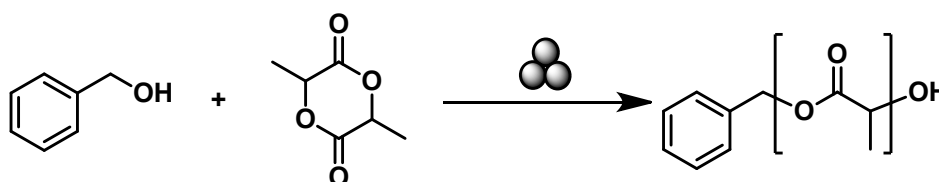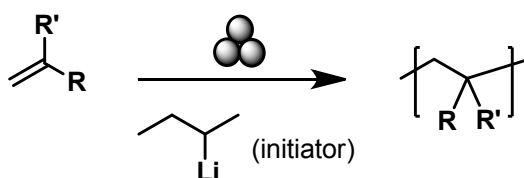
Radical Polymerizations

Kargin (1959)
Oprea (1980s)
Kuzuya (1990s)
Bielawski (Controlled, 2020)

Ring-Opening Polymerizations

Kim (2017)
Giani (2021)

Anion-initiated Polymerizations

This work

**Anionic initiation
Radical propagation**

Figure 1. Brief summary of mechanochemical chain polymerizations.

Journal Name   **ARTICLE**

Results and discussion

Ball-milling Anionic Polymerizations: Avoiding Radical Initiation

Polymerization of vinyl monomers, such as styrene and (meth)acrylate, constitutes the largest portion of polymer production. Mechanochemists have also paid attention to vinyl polymerization, anticipating a fast rate and green chemistry. An initial trial by Kagan et al. revealed that grinding monomers by ball-milling promotes polymerization.[6a-d] Later studies by Oprea and Kuzuya realised that ball-milling vinyl polymerization is a radical process and does not require a radical initiator.[6e-i] They proposed a free radical polymerization mechanism involving electron release and transfer from the milling materials upon high-energy collisions.[6e,h] However, self-initiation of the monomers may also be possible.[5,12]

When ionic polymerization is performed in a mechanochemical ball-milling system, a competing radical process should not occur. Thus, we employed low-energy ball-milling conditions under which radical initiation does not occur. Under these conditions, only highly reactive anionic species would trigger polymerization (Table 1). Two solid monomers, 4-vinyl biphenyl (4-VBP) and 4-biphenyl methacrylate (4-BPMA), were polymerized, representing the styrenic and methacrylate species, respectively. Each vinyl compound was milled with various balls at various vibration frequencies. Many ball-milling studies have employed stainless steel containers and balls because of their high density (high energy) and economy.[5] However, metallic stainless steels can easily release electrons and facilitate radical generation. Therefore, herein, ceramic zirconia jars and balls of lower density were employed, with the expectation of less radical-initiated polymerization. 4-VBP or 4-BPMA (100 mg) was added to a 10 mL zirconia milling jar with two zirconia balls with diameters of 8 mm under inert conditions. The vessel was assembled and placed in a vibratory ball-mill (Retsch MM400). After an hour at a frequency of 30 Hz, proton nuclear magnetic resonance (^{1}H NMR) spectroscopy analysis with CH_2Br_2 as an internal standard revealed quantitative polymer formation: 99% for 4-VPM and 95% for 4-BPMA (entry 1). To mitigate undesirable radical processes, the energy was further reduced. At a vibrational frequency of 20 Hz, radical polymerization was significantly retarded (entry 2). Only 27% of 4-VBP participated in the polymerization, whereas 4-BPMA remained unreacted.

The effect of the ball size was further evaluated, as this parameter exerted a profound effect in our previous studies on the ring-opening polymerization of lactides.[7a] At 20 Hz, 4-BPMA remained unreacted regardless of the ball size, but 4-VBP conversion was sensitive to the scale of impact (entries 3 and 4). With a single 10 mm ball, 71% of 4-VBP was converted to the corresponding polymer. With 5 mm balls (8 ea), there was no conversion to the polymer. Because the 5 mm balls did not initiate the polymerization of either 4-VBP or 4-BPMA at 20, 25, and 30 Hz (entries 4–6), the anion-initiated polymerization was evaluated with 5 mm balls in the ensuing reactions.

Table 1. Mechanochemical radical polymerization of 4-VBP and 4-BPMA without an external initiator[a]
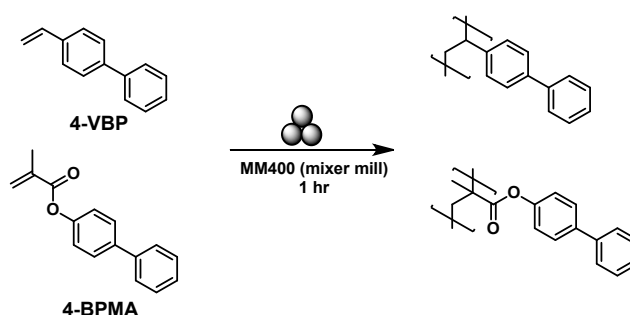
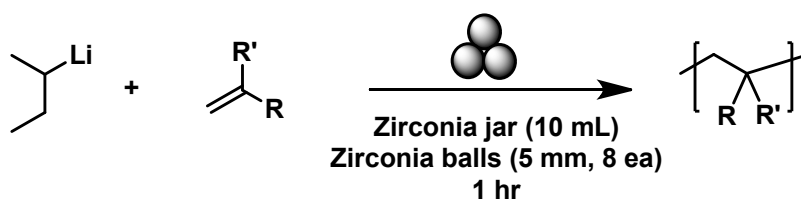| Entry	Container	Balls	Hz	Conv. (%)[b]	
				4-VBP	4-BPMA
1	Zirconia (10 mL)	Zirconia, 8 mm, 2 ea	30	99	95
2	Zirconia (10 mL)	Zirconia, 8 mm, 2 ea	20	27	< 1
3	Zirconia (10 mL)	Zirconia, 10 mm, 1 ea	20	71	< 1
4	Zirconia (10 mL)	Zirconia, 5 mm, 8 ea	20	<1	< 1
5	Zirconia (10 mL)	Zirconia, 5 mm, 8 ea	25	<1	< 1
6	Zirconia (10 mL)	Zirconia, 5 mm, 8 ea	30	<1	< 1

[a]Average values from two experiments. [b]Determined by ^{1}H NMR spectroscopy with CH_2Br_2 as an internal standard

Alkyl Lithium-initiated Polymerization – Anionic initiation and radical propagation

To evaluate the mechanochemical anionic polymerization, a widely used initiator, secondary butyl lithium (*s*-BuLi), was applied to solid 4-VBP or 4-BPMA (Table 2). Commercial *s*-BuLi (1.4 M solution in cyclohexane) was used. The use of solid *s*-BuLi was initially attempted, but the poor reproducibility of the reaction prompted us to use this solution. The monomer and *s*-BuLi were added to a 10 mL zirconia jar with eight zirconia balls of 8 mm diameter. All polymerizations were assembled under inert atmosphere in a dry box and moved to a mixer mill (MM400) at 30 °C.

First, the monomer to initiator ratio ([M]/[I]) was examined for [M]/[I] = 25, 50, and 100 (entries 1−6). All reactions produced the corresponding polymers. Because this condition does not promote radical initiation, the products are from anionic initiation. A lower initiator loading resulted in less conversion, proving the direct involvement of *s*-BuLi in the initiation step. However, molecular weight analysis by size exclusion chromatography (SEC) indicated that mechanochemical anionic polymerization may not be living polymerization. Well-controlled anionic polymerization is expected to afford precise control of the product size and distribution, where 1) the monomer consumption is linearly related to the initiator and molecular weight (or polymer chain length) and 2) the product exhibits narrow dispersity ($Đ$).[10,13] However, the mechanochemical reaction did not follow this trend. The expected degree of polymerization (DP_{exp}), which is the amount of reacted monomer per initiator, was poorly correlated with the number-average molecular weight (M_n) (Figure 2). In the case of 4-VBP, as DP_{exp} moved from 25, to 42 to 54, the M_n increased exponentially from 12.6 kg/mol to 40.7 kg/mol to 105 kg/mol, respectively (entries 1−3). For 4-BPMA, a 76% increase in DP_{exp} from 25 to 44 resulted in marginal chain extension (M_n moved from 42.0 kg/mol to 45.3 kg/mol (entries 5 and 6)). In addition, all polymerizations exhibited large dispersity. These results suggest that the kinetics established for living anionic polymerization are not valid under solid-state ball-milling conditions.

The effect of the vibrational frequency was investigated (entries 7−12). Higher frequencies resulted in higher conversions of both 4-VBP and 4-BPMA owing to better mixing and higher energy input. Poor reproducibility was observed in the case of 4-VBP at 20 Hz (entry 9). Two polymerizations were conducted simultaneously and produced a large discrepancy in M_n (40.7 kg/mol and 135 kg/mol), respectively. In general, 4-BPMA showed lower reactivity than 4-VBP, and low-energy conditions did not promote measurable conversions to the polymers (entries 11 and 12).

Table 2. Polymerization of 4-vinyl biphenyl with *s*-BuLi initiator[a,b]

Entry	Monomer	Hz	[M]/[I]	Conv. (%)[c]	DP$_{exp}$[d]	M_n (kg/mol)[e]	$Đ$[e]
				[M]/[I] variation set			
1		30	25	99	25	12.6	1.92
2	4-VBP	30	50	83	42	40.7	2.43
3		30	100	54	54	105	2.56
4		30	25	73	18	35.6	1.75
5	4-BPMA	30	50	50	25	42.2	1.81
6		30	100	44	44	45.3	1.88
				Vibration energy variation set			
7		30	50	83	42	40.7	2.43
8	4-VBP	25	50	54	27	44.9	2.60
9		20	50	18	9	47.0/135	4.46/2.29
10		30	50	50	25	42.2	1.81
11	4-BPMA	25	50	<5	-	-	-
12		20	50	<1	-	-	-

[a]Average values from two experiments. [b]*s*-BuLi solution (1.4 M in cyclohexane) was used. [c]Determined by ^{1}H NMR spectroscopy with CH$_2$Br$_2$ as an internal standard. [d]DP$_{exp}$=[M]/[I] X conversion. [e]Determined by SEC calibrated with polystyrene standards in tetrahydrofuran (THF) at 40 °C.
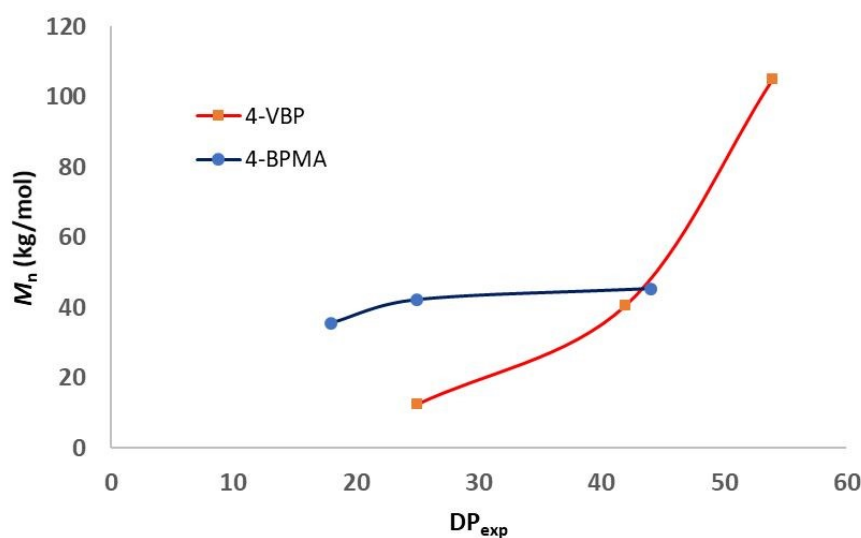
Figure 2. Plot of DP$_{exp}$ vs. M_n for 4-VBP and 4-BPMA (Table 1, entries 1–6).

To understand the details of the polymerization process, we monitored the trends in the molecular weight (M_n) and dispersity ($Đ$) as polymerization proceeded (0.10 g of 4-BPMA, [M]/[I] =50, eight 5 mm balls with 10 mL zirconia jar, 30 Hz, Figure 3). The monomer consumption was slow at the initial stage when alkyl lithium played an initiator role. After 10 min, no polymeric products were detected by ^{1}H NMR and SEC. After 20 min, the mixture contained a measurable amount of polymer (1% conv., M_n = 51.3 kg/mol, $Đ$ = 1.10). Despite the small conversion, a high-molecular-weight polymer was obtained with narrow dispersity. The molecular weight continued to increase up to 30 min (6% conv., 61.3 kg/mol, $Đ$ = 1.50). However, the increase in the molecular

weight did not follow this conversion. A sharp decrease in M_n was also observed, whereas the slope of the plot representing the increase in rate doubled after 40 min. The dispersity became broader. After 90 min, near-quantitative monomer consumption, despite continuous M_n reduction, was observed. The molecular weight reached 20.4 kg/mol at 120 min, which is one-third of the maximum M_n.
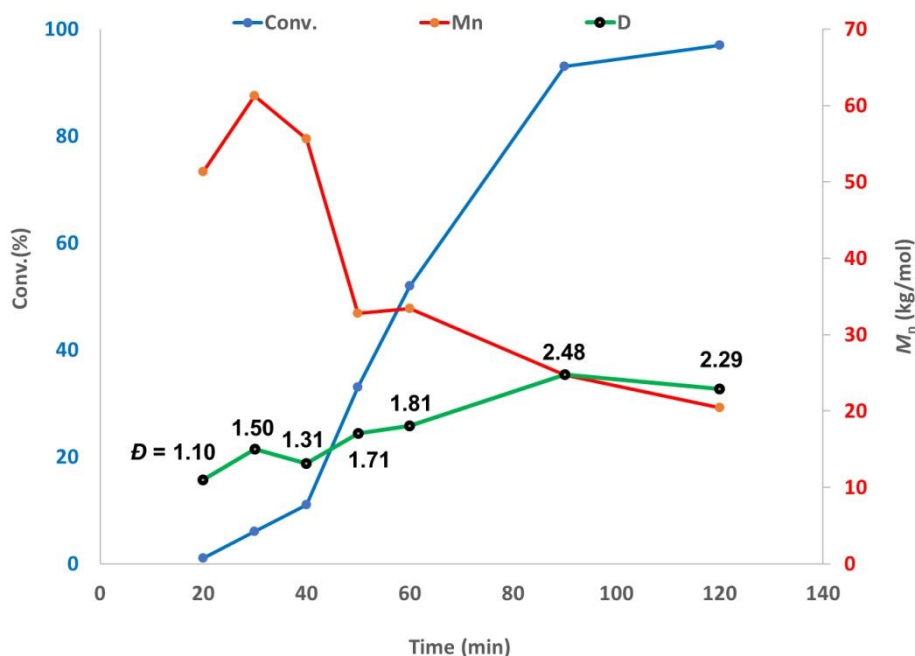
Figure 3. Plot of the polymerization time vs. conversion, number-average molecular weight, and dispersity. [4-BPMA (0.10 g), [M]/[I] = 50 in zirconia jar (10 mL) with eight zirconia balls (5 mm)].

Concurrent chain growth and degradation under ball-milling conditions have been reported in prior mechanochemical radical and ring-opening polymerizations. The overall observed trend of the anion-initiated polymerization was similar to that of the mechanochemical radical polymerization reported by Kuzuya.[6h-j] The initial polymers were clearly obtained from *s*-BuLi initiation. A highly reactive secondary alkyl anion is buried in a 4-BPMA particle, and the high monomer concentration probably explains the high-molecular-weight product detected at 20 min. The narrow dispersity also supports anionic polymerization. The high-molecular-weight product, and thus the stiff polymer chain, subsequently underwent chain degradation during ball-milling.[14] Fragmentation generates macroradicals and polymeric chains with a radical end, thereby promoting chain propagation. As more polymer chains are formed, chain degradation occurs more frequently; thus, the number of macroradicals increases. At this stage, radical propagation dominated anionic propagation, and overall monomer consumption was also accelerated.

To prove the involvement of this radical process, a selective anion-quenching experiment was performed (Figure 4). After 50 min of *s*-BuLi-initiated polymerization, a portion of a protic liquid, herein water (40 µL), was added, which selectively quenched the alkyl anions. The mixture was placed in MM400 for further milling for 40 min. After 50 min of ball-milling with *s*-BuLi (mixture A), 41% of the intermediate was converted to the polymer (M_n = 47.2 kg/mol). Although water is expected to quench the alkyl anions, the polymerization process proceeded further, which may indicate macroradical-mediated radical propagation. Mechanical fracture resulted in a lower molecular weight product than that from mixture A (mixture B, M_n = 12.7 kg/mol).
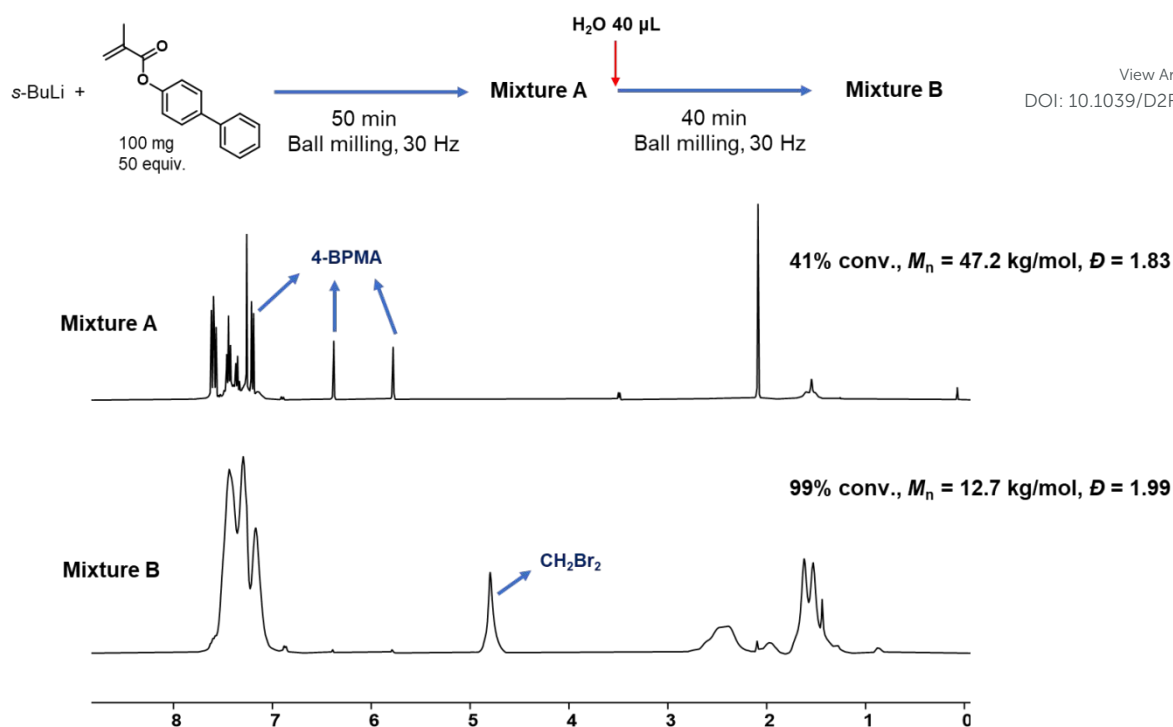
Figure 4. Procedure employed in anion quenching experiments and ^{1}H NMR spectra and M_n data for mixtures A and B.

Tacticity analysis also supported radical propagation (Figure 5). The ^{13}C NMR peak of the carbon in the α-position relative to the carbonyl group of three poly(4-BPMA) samples provided triad and dyad distributions: A) mechanochemical radical process (MM400, no initiator), B) mechanochemical anion-initiated polymerization after 60 min, and C) after 120 min.[15] All three samples exhibited syndiotactic-rich structures with approximately 60% racemic(r) dyads and over 40% meso(m) dyads. Anion-initiated mechanochemical polymerization (Figure 5B and 5C) produced microstructures identical to those obtained via mechanochemical radical polymerization (Figure 5A). The anion-initiated polymerization of 4-BPMA followed a propagation mechanism similar to that of the radical pathway. The polymer structures obtained after 60 min (56% conv.), and 120 min (97% conv.) were almost identical. The same radical propagation process continued throughout the polymerization process.
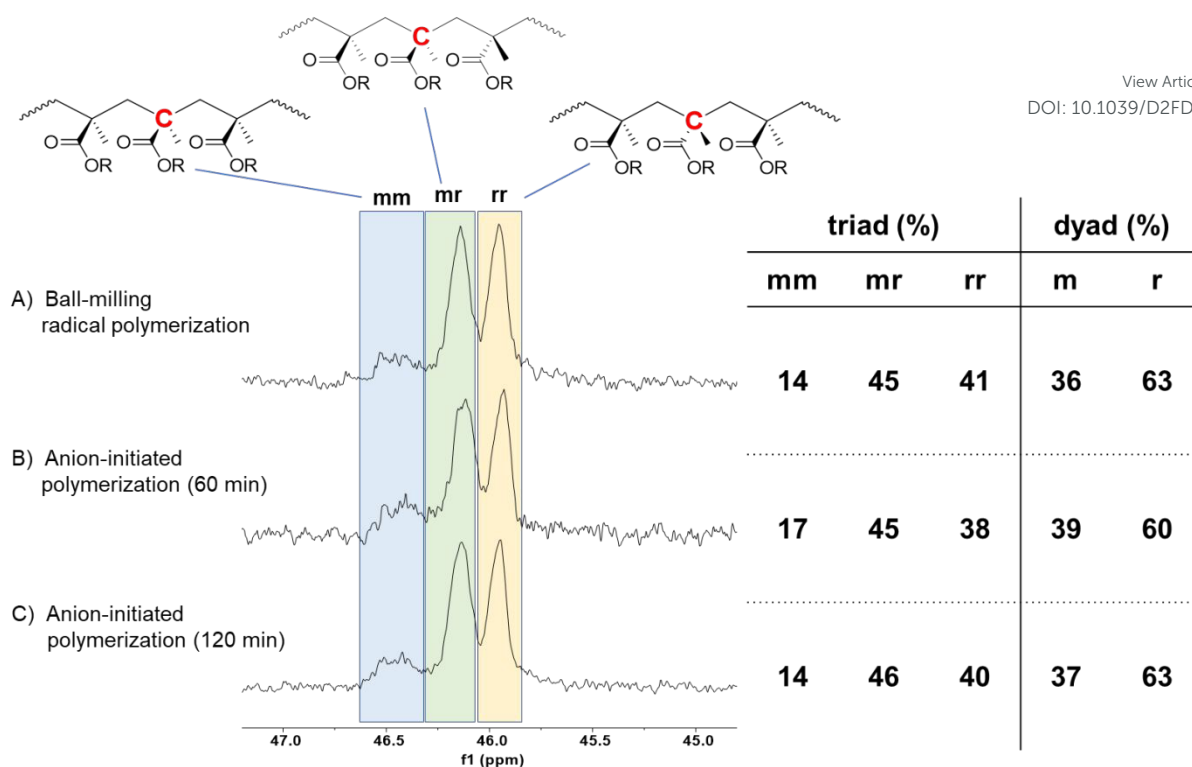
	triad (%)			dyad (%)	
	mm	mr	rr	m	r
A) Ball-milling radical polymerization	14	45	41	36	63
B) Anion-initiated polymerization (60 min)	17	45	38	39	60
C) Anion-initiated polymerization (120 min)	14	46	40	37	63

Figure 5. Comparison of stereoselectivity of different polymerization processes.
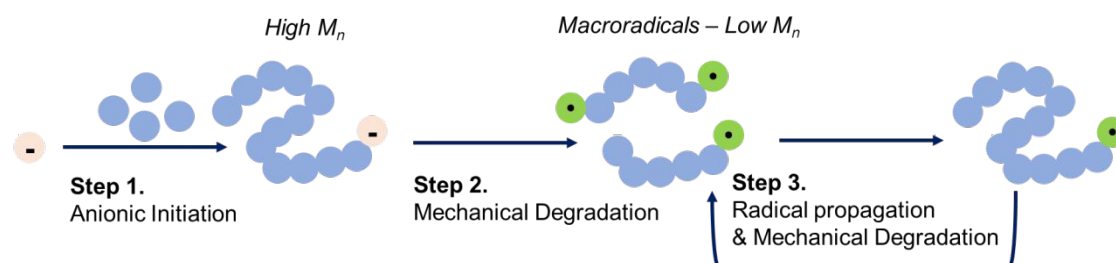
Conclusions

Figure 6. Schematic of anion-initiated mechanochemical polymerization: Anionic initiation and radical propagation.

Anionic polymerization, one of the most fundamental vinyl polymerizations, was performed under solid-state mechanochemical conditions. Polymerization of the vinyl monomer and alkyl anion initiator proceeded via anion initiation and radical propagation processes (Figure 6). The popular initiator *s*-BuLi successfully initiated the polymerization of styrenic and methacrylic monomers under conditions in which radical initiation was completely suppressed (step 1). Early anionic propagation produced a long polymer chain. Mechanical degradation of the resulting polymer chain generated macroradicals, a unique product of the mechanochemical process (step 2). Upon continuous macroradical feeding, radical chain propagation becomes dominant over anionic propagation. The concurrent radical propagation and chain degradation of macroradicals define the overall process (step 3). Time-resolved ^{1}H NMR/SEC and ^{13}C NMR microstructural analyses supported these results. This example indicates that the classical kinetics obtained in solution polymerization should be re-evaluated under solid-state ball-milling conditions. Further development for precise mechanochemical polymerization is in progress.

Experimental

General considerations

All the polymerization reactions were performed in a glove box to avoid contamination with air and moisture. *s*-BuLi and 4-VBP were used as-received. 4-BPMA was synthesised according to a previously reported method. A Retsch Mixer Mill MM 400 instrument was used for the ball-milling experiments.

Measurement

^{1}H and ^{13}C NMR spectra were obtained using a Bruker Avance III HD Fourier-transform 400 MHz NMR spectrometer and referenced to the residual protonated solvent. SEC analyses with refractive index (RI) detection were used to determine the number-average molecular weight (M_n) and dispersity ($Đ$). RI measurements were carried out using an instrument composed of a Waters 1515 isocratic pump, 2414 differential refractive index detector, and column-heating module with Shodex HK-403 and HK-404L columns placed in series. The columns were eluted with THF (preservative-free HPLC grade, Daejung Chemical Company) at 40 °C at 0.5 mL min^{-1} and were calibrated using 16 monodisperse polystyrene standards (Alfa Aesar).

Representative anion-initiated polymerization of 4-BPMA (Table 2, entry 5)

4-BPMA (0.10 g, 50 equiv.) and *s*-BuLi (6 µL, 1.4 M in cyclohexane, 1 equiv.) were added to a zirconia milling jar (10 mL), followed by the addition of zirconia balls (8 ea, 5 mm diameter). The tightly sealed vessel was placed in a vibrational ball-mill and subjected to 30 Hz vibration milling for an hour. The milling vial was then opened, and the internal standard CH_2Br_2 (20 µL) was added. A portion of the resultant white powder was subjected to ^{1}H NMR spectroscopy and SEC measurements to determine its conversion and molecular weight. The average of the two experiments is reported. 50% conversion; SEC data (THF, PS standard): M_n = 42.2 kg mol^{-1}, $Đ$ = 1.81.

Conflicts of interest

There are no conflicts to declare

Acknowledgements

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