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Mechanochemical Synthesis of Poly(phenylene vinylenes)

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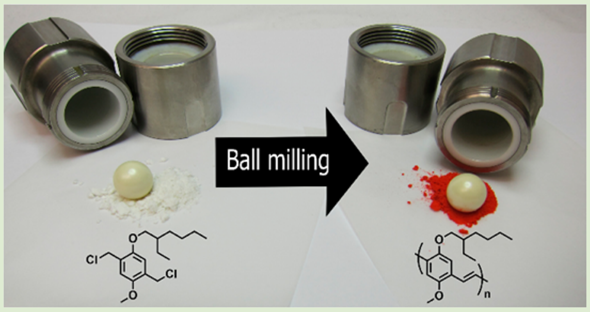
Supporting Information

ABSTRACT: We report a simple, rapid, and solvent-free methodology for solid-state polymerizations yielding poly(phenylene vinylenes) (PPVs) promoted by ball-milling. This solid-state Gilch polymerization method produces PPVs in as little as five minutes of milling. Detailed investigations of the parameter space governing the solid-state polymerization, i.e., milling time, base strength, solid-state dilution, milling frequency, and size of milling balls, revealed that polymerization by ball-milling is a rapid process achieving molecular number average weights of up to 40 kDa in up to 70% yield. To explore the scope, a solid-state polymerization via the dithiocarbamate precursor route is explored.



Application of mechanical force as activation for chemical transformations, i.e., mechanochemistry, is a powerful alternative to photo-, electro-, or thermochemical activation.[1] The impact of mechanochemistry on organic synthesis is now recognized, and many important organic transformations have been successfully demonstrated, e.g., amide couplings,[2] palladium-catalyzed cross-couplings,[3] and the Wittig reactions.[4] Several informative reviews have been recently published covering these developments.[5] Solid-state transformations, typically promoted by ball-milling, have several advantages over their traditional "wet-chemistry" counterparts. First, the reactions can proceed in high yields with short reaction times. Second, no solvents or reagent equivalent solvents are added, which significantly reduces waste generation. Despite demonstrations of mechanochemical activation in organic synthesis, the utilization for synthesis of polymers, especially conjugated polymers, is largely untapped. There have only been a handful of reports on the synthesis of conjugated polymers by mechanochemical-promoted polymerizations.[6] A critial element in polymer synthesis is the fact that mechnochemical treatments are well-known to break polymers down and can be used to lower their molecular weights. As a result, investigations of mechanochemical parameters (i.e., reaction time, energy input, dilution of the monomers, etc.) need to be examined to determine the potential of this method in polymer synthesis. Detailed investigations of the parameter space governing solid-state polymerization provide new insight and allow further utilization of this solid-state synthesis method.

We report herein a simple, rapid, and solvent-free method for the synthesis of poly(phenylene vinylene) via solid-state polymerization promoted by ball-milling and the parameters influencing the mechanochemical-promoted polymerization. Poly(phenylene vinylene)s (PPVs) have received extensive research interest since their use as an electroluminescent material in the early 1990s.[7] PPVs can be synthesized by methods including Wessling,[8] sulfinyl,[9] xanthate,[10] dithiocarbamate,[11] Gilch,[12] Wittig,[13] Heck,[14] and Suzuki[15] couplings. The Gilch method is the preferred route to PPVs as a result of the easily obtainable monomer and straightforward reaction conditions producing conjugated polymers of high molecular weight in good to excellent yield.[16] However, the Gilch method still has drawbacks. First, to achieve high yields extended reaction times approaching 24 h are typically required. Second, the reactive quinodimethane intermediates undergo fast polymerization, and associated high molecular weight fractions often lead to gelation of the reaction mixture, which complicates purification.[16] We envisioned that these issues could be resolved by utilizing a solid-state Gilch polymerization promoted by ball-milling.

To probe the possibilities of solid-state Gilch polymerization and to investigate the parameter space of the solid-state mechanochemical polymerization, we selected poly(2-methoxy-5-2′-ethylhexyloxy phenylene vinylene) (MEH-PPV) as a model system.[17] MEH-PPV is among the most widely studied PPVs, owing to the excellent solubility in most organic solvents. The required monomer for the synthesis of MEH-PPV via Gilch polymerization is readily synthesized in a multigram scale via a two-step procedure.[18]

In our initial attempt at solid-state Gilch polymerization promoted by ball-milling, the MEH-PPV monomer and three equivalents of potassium *tert*-butoxide were added to a 10 mL zirconium oxide milling jar along with a 10 mm diameter zirconium oxide ball. The solid reaction mixture was subjected to vibrational ball-milling in a Retsch mixer-mill 400 at 30 Hz for 30 min. After ball-milling, quenching was achieved by adding acidified methanol (5 mL) to the milling jars and

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subjecting the slurry to 15 s of ball-milling to ensure complete quenching of the polymerization reaction. This direct quenching procedure eliminates any continued polymerization that may occur during workup, allowing us to probe exclusively the degree of polymerization taking place during ball-milling. The red slurry was poured onto a filter and washed thoroughly with water and methanol. The obtained red powder (see Figure 1) was subsequently dissolved in chloroform, precipitated from methanol, and subjected to gel permeation chromatography (GPC) analysis using a polystyrene standard. This confirmed that ball-milling yielded a polymeric material; i.e., a number average molecular mass (M_n) of 35 kDa was obtained for the product. The usage of zirconium oxide milling jars was chosen as the ceramic properties allow for the important direct quenching procedure as opposed to use of stainless steel milling jars, which are not inert toward the acidic quenching conditions.

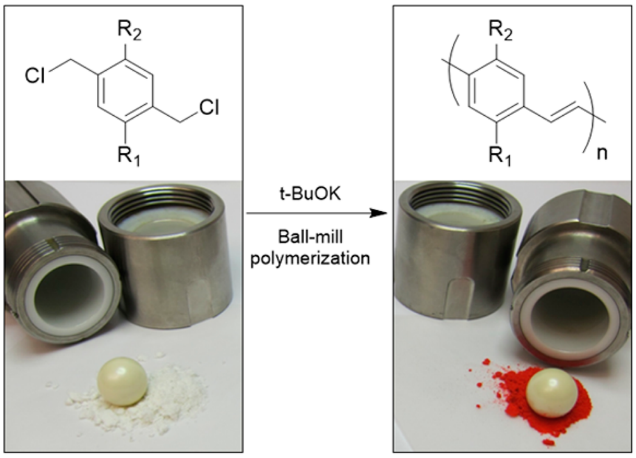


Figure 1. Solid-state Gilch polymerization promoted by ball-milling.

The success of our initial experiment with solid-state Gilch polymerization prompted a series of questions: What is the effect of milling time on polymer size, polydispersity, and yield? Does the solid-state nature of the polymerization alter the base requirements? How does solid-state dilution of the monomer in the base affect the polymer size, polydispersity, and yield? What is the required energy input for successful polymerization? To answer these questions we initiated an investigation into the parameter space governing the solid-state Gilch polymerization: milling time, base strength, solid-state dilution, milling frequency, and size of the milling balls. All experiments described in the following were repeated either two or four times, and presented results (yields, polydispersity index (PDI), and M_n) are reported as averaged values.

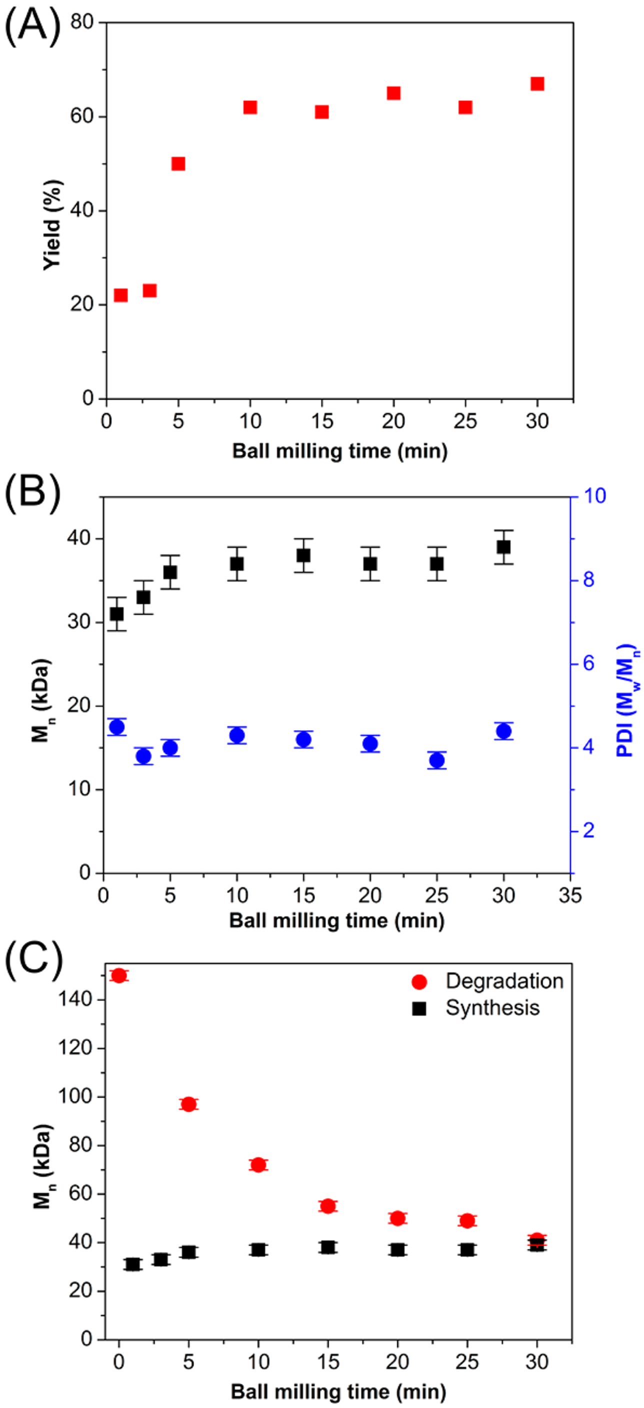
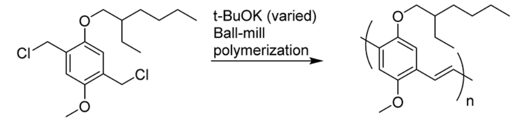


Figure 2. Effect of varying milling time on isolated yield, molecular number average weight (M_n), and polydispersity (PDI). (A) Isolated yield as a function of milling time. (B) M_n and PDI as a function of milling time. (C) M_n as a function of milling time for synthesis (black squares) of solid-state prepared MEH-PPV and degradation (red circles) of solution-prepared MEH-PPV.

First, we conducted a series of solid-state polymerizations with varying milling time. The isolated yield, along with molecular weight and polydispersities estimated by GPC using a polystyrene standard, are shown in Figure 2. The solid-state Gilch polymerization promoted by ball-milling is rapidly occurring; i.e., after just five minutes, polymers with M_n of 35 kDa are obtained in >50% yield (Figure 2A). A significant improvement in isolated yield as a function of ball-milling time is observed; however, the main improvement occurs at short milling times, i.e., one to five minutes, with isolated yields increasing from 22 to 50%. After ten minutes of ball-milling the isolated yield reaches 63% with only a minor improvement upon extended milling times, e.g., 67% at 30 min. It should be noted that during the purification process precipitation of small amounts of insoluble polymeric material was discarded. The insoluble material may originate from cross-linking of the polymer chains during the radical polymerization at very high concentrations. Surprisingly, only a minor correlation between milling time and the molecular weight is observed, with M_n rapidly reaching a plateau of $\sim$40 kDa (Figure 2B). The isolated polymers show a broad molecular weight distribution with polydispersity ranging from 3.8 to 4.5 with no significant improvement with increased milling time.

To gain further insight into the observed upper limit of $M_n \sim$ 40 kDa for the isolated polymers, a MEH-PPV with a $M_n \sim 150$ kDa prepared by standard solution-based methods[16] was subjected to ball-milling, and samples were taken at specific milling times, i.e., 5, 10, 15, 20, 25, and 30 min. The samples were analyzed by GPC, and the data are depicted in Figure 2C. The M_n's of the solid-state polymerization from Figure 2B are shown in Figure 2C for comparison. We observe a rapid degradation of MEH-PPV as a function of milling time; i.e., after 15 min of ball-milling the M_n is only 1/3 of the starting value. The results further show that the majority of degradation takes place within the first 15 min of milling after which M_n levels off to a plateau at ~40 kDa. We hypothesize, based on this observation, that when the M_n of the PPVs exceeds 40 kDa the polymer chain can accumulate sufficient energy for chain scission; i.e., degradation occurs. The correlation between the M_n for the degradation and the synthesis suggests that two processes occur during ball-mill promoted polymerization, i.e., a constructive and destructive process. For polymer chain sizes of $M_n < 40$ kDa the constructive process is dominant, while the destructive pathway becomes the dominant pathway for large polymer chains. A similar trend has been reported for the mechanochemical synthesis/degradation of styrene/polystyrene.[19] It should be noted that once chain scission has occurred the polymer chain loses its ability to reinitiate polymer growth. This is supported by the lack of improvement in PDI as a function of milling time. In the characterization of the MEH-PPVs obtained from our mechanochemical method, we observe no significant differences between solid-state prepared and solution-prepared polymers by FT-IR and ^{1}H NMR, and the polymers have similar degradation temperatures as evaluated by thermogravimetric analysis (see Supporting Information (SI)).

The solid-state nature of this method results in very high concentrations of monomers compared to solution-based reactions; i.e., in the solid-state mixture approximately 1/4 of the total volume is monomer. Addition of additional base effectively constitutes a dilution of the monomer. To investigate the effect of solid-state dilution, we conducted a series of polymerizations with varying amounts of base ranging from 1 to 20 equiv. The results from this series of experiments are depicted in Figure 3. In a typical Gilch polymerization carried out in solution 3 to 4 equiv of *t*-BuOK is added to initiate effective polymerization. We observe a similar requirement for the solid-state Gilch polymerization; i.e., no polymerization is observed when adding only one or two molar equivalents of *t*-BuOK, and only small molecule products are isolated. Addition of >3 equiv of base results in polymerization. Interestingly, the yield of the polymerization increases significantly with increasing amount of base; i.e., only 20% yield is obtained at 3 equiv of base, while a very satisfying 72% isolated yield is obtained at 10 equiv of base. Further dilution, as illustrated by 20 mol equiv of base, has a severe impact on the isolated yield, and only 35% is obtained in this case. We speculate that the beneficial effect up to around 10 equiv is due to minimization of cross-linking by dilution and that increased dilution beyond this point results in less efficient polymerization. Again, no significant effect on M_n is observed as a function of equivalent base added. We analyzed the samples from this series of experiments by UV−vis spectroscopy (see Figure 3, bottom). This further confirms that the number of base equivalents affects the polymerization. For low molar equivalents, i.e., 1 or 2 equiv, we observe absorption peaks at high energy corresponding to short conjugated systems. As we increase the molar equivalents of base the main absorption peak shifts toward the characteristic major absorption peak of MEH-PPV, as illustrated by comparison to a solution-prepared MEH-PPV. This trend can even be observed by simple inspection of the visual colors of the crude polymers (see SI). Furthermore, as Balemo et al. have reported effective ylide formation in the solid-state promoted by ball-milling utilizing milder bases than the corresponding solution-based reaction,[4] we tested K_2CO_3, KOH, and *t*-BuOK as bases for our solid-state Gilch polymerization. Unfortunately, no polymerization was observed for the milder bases, K_2CO_3 and KOH, under the tested conditions.



Base (eq.)	M_n (Kda)	PDI	Yield (%)
1	N/A	N/A	23
2	N/A	N/A	22
3	35	3.4	20
4	38	3.8	36
6	36	4.0	50
10	30	4.8	72
20	40	7.9	35

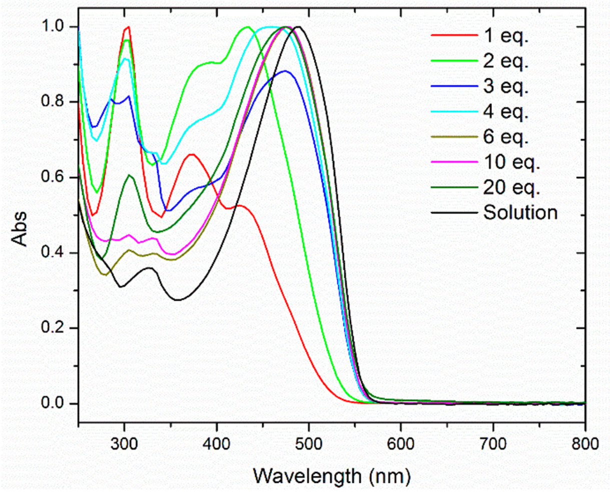


Figure 3. Effects of varying the equivalents of *t*-BuOK illustrated by GPC analysis (top) and UV−vis data (bottom).

Lastly, we investigated the requirements on the energy input for effective polymerization. This was achieved by changing the vibrational milling frequency as well as the size of the milling balls. In our investigations of the effect of ball milling frequency (number of impacts between ball and vial wall per second), we conducted solid-state polymerizations at 5, 10, 15, 20, 25, and 30 Hz (see Table 1). At low frequencies, i.e., 5 and 10 Hz, no significant polymerization occurs, while increasing the frequency to 15 Hz results in inhomogeneous polymerization arising from insufficient mixing. Higher frequencies result in successful polymerization with improved M_n and isolated yields

Table 1. Effects of Frequency (Top Table) and Size of the Milling Balls (Bottom Table)

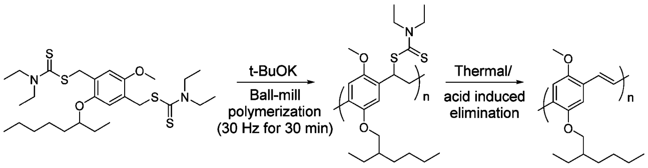
Frequency (Hz)	M_n (kDa)	PDI	yield (%)
<10	-	-	-
15	inhomogeneous	inhomogeneous	-
20	28	8.2	28
25	24	4.4	45
30	39	4.4	67
ball size (mm)	**M_n (kDa)**	**PDI**	**yield (%)**
1.5 (68 pcs)	-	-	-
5 (10 pcs)	inhomogeneous	inhomogeneous	-[a]
10 (1 pcs)	39	4.4	67

[a] The obtained samples were inhomogeneous as a result of incomplete mixing, and as a result M_n, PDI, and yield were not determined.

as we increase the frequency from 20 to 30 Hz, the upper frequency limit of the instrument. These results suggest that solid-state polymerization promoted by ball-milling requires a certain amount of energy to promote monomer activation as well as effective mixing. We speculated that utilizing milling balls with a smaller diameter would improve polymerization due to improved mixing. To test this hypothesis we conducted a series of polymerizations with varying sizes of milling balls, i.e., diameters of 1.5, 5, and 10 mm. For these experiments, we kept the total mass of added milling balls constant, to ensure approximately the same overall energy input in each polymerization. The results are summarized in the bottom part of Table 1. We observed no polymerization with the smallest diameter milling balls (1.5 mm), and only inhomogeneous pockets of polymerization are observed for milling balls with diameter of 5 mm. These results suggest that solid-state Gilch polymerization via vibrational ball-milling requires a threshold impact energy in addition to efficient mixing; i.e., the most important contribution to successful polymerization stems from impact energy, and in our system milling balls of 10 mm diameter are required to ensure sufficient energy to effectively initiate and promote polymerization. Here, it should be noted that milling jars did not appear to heat up (determined by touch) during these short milling experiments. To confirm that successful solid-state polymerization is not a result of impact heating, we subjected a solid mixture of monomer and *t*-BuOK to heat in an oil bath. We observed that polymerization does occur when the sample is subjected to prolonged heating (1 h) at 100 °C. However, the polymerization results in heavy cross-linking and soluble polymer were only isolated in 10% yield. This emphasizes the importance of simultaneously inducing high impact energy and efficient mixing to achieve successful solid-state polymerization.

The successful solid-state Gilch polymerization results in broad PDIs ranging from 3.5 to 4.5. In solution-based polymerization of PPVs, the broad PDIs associated with the Gilch polymerization can be avoided by utilizing a precursor route, such as sulfinyl,[9] xanthate,[10] and dithiocarbamate[11] (Scheme 1). We were interested in investigating if the improved characteristics of the precursor strategies would translate to our solid-state polymerization methodology. To this end we converted the Gilch monomer to the corresponding dithiocarbamate monomer in one simple step (see SI) and subjected this monomer and 10 equiv of *t*-BuOK to our optimized solid-state polymerization conditions, i.e., 30 min at 30 Hz. In solution-based dithiocarbamate polymerizations a precursor polymer is first isolated and subsequently converted to the final conjugated PPV by thermal or acid elimination. This strategy typically requires the use of very strong lithium bases, such as LHMDS, to produce the desired precursor polymer.[11] Much to our delight, we observe that a polymeric product can be obtained by utilizing milder base, here *t*-BuOK, under ball-mill-promoted polymerization. The obtained polymers are of comparable molecular weight to MEH-PPV obtained by solid-state Gilch polymerization, namely, M_n of 35 KDa. Moreover, this solid-state method provided a precursor polymer with a relatively low PDI of 1.4 in 54% isolated yield. The presence of the diethyl-thiocarbamate moiety was confirmed by ^{1}H NMR (see Supporting Information). Furthermore, thermal elimination was observed at 180 °C during thermogravimetric analysis, which is in good agreement with temperatures for thermal elimination of such PPV−precursor polymers reported in the literature.[11]

Scheme 1. Dithiocarbamate Route Promoted by Ball-Milling



In summary, we demonstrated successful solid-state polymerizations mechanochemically promoted by ball-milling. This method offers a rapid, simple, and solvent-free synthetic route to PPVs. Detailed investigations of parameters affecting the solid-state polymerization revealed that polymers with molecular weights up to 40 kDa are produced in as little as five minutes. The isolated yield of the solid-state polymerization is affected both by milling time and more importantly by solid-state dilution, with a 44% improvement in yield by increasing the amount of base from six to ten equivalents. An upper limitation for the molecular weight of the polymers, ~40 kDa, was observed and ascribed to competing mechanochemical constructive and destructive processes. Furthemore, the solid-state dithiocarbamate precursor route resulted in polymers with a PDI of 1.4 constituting a significant improvement over the solid-state Gilch polymerization. The solid-state nature of this methodology could allow for direct synthesis of PPVs from monomers that are incompatible with solution-based reaction conditions for the Gilch polymerization. Furthermore, we envision that this methodology will find utility in the fabrication of composite materials in which one component has poor solubility in organic solvents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, NMR, UV−vis, GPC, and related details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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