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Complete List of Authors:	Balema, Viktor; Iowa State University, Ames Laboratory; Ames Laboratory Hlova, Ihor; Iowa State University, Materials Science and Engineering Carnahan, Scott; Iowa State University, Department of Chemistry; Ames Laboratory, Seyedi, Mastooreh ; Clemson University College of Engineering and Sciences Dolotko, Oleksandr; Ames Laboratory, Division of Materials Science & Engineering Rossini, Aaron; Iowa State University, Department of Chemistry; Ames Laboratory, Luzinov, Igor; Clemson University, School of Materials SandE

COMMUNICATION

Depolymerization of polystyrene under ambient conditions

Viktor P. Balema,*[a] Ihor Z. Hlova,[a] Scott L. Carnahan,[a,c] Mastooreh Seyedi,[b] Oleksandr Dolotko,[a] Aaron J. Rossini[a,c] and Igor Luzinov*[b]

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Depolymerization of the addition polymer polystyrene to monomeric styrene is facilitated by mechanochemical processing at room temperature under ambient atmosphere. The reaction occurs in metal-based milling media in concert with scission of macromolecular chains that generates carbon-centered free-radicals detectable by EPR spectroscopy, even though the processing is performed in air.

A circular economy is a closed-loop economic system that holds strong promise for reducing waste streams and preventing depletion of critical resources via recycling, repair, reuse, remanufacturing, and upcycling of goods that have reached the end of their useful life.[1] Currently, about 85% of the materials generated world-wide end up in landfills or incinerators[2] – an enormous waste of valuable resources that causes severe distress for natural ecosystems due to the release of hazardous substances into the environment.[3] Plastics represent a considerable fraction of discarded materials and, according to the recent estimates,[4] more than 100 million metric tons of polymers are annually produced worldwide; most of them (i.e.~ 90% in the USA) are tossed away as soon as their useful life is over. Given the fact that most applications require chemically stable and durable polymers, it is not surprising that plastic waste does not easily degrade in landfills. To stop the growing flood of polymer waste, plastics must be recycled or converted into new value-added products, or burned up for energy, which produces carbon dioxide and other hazardous gases. Currently, the main approaches to plastic recycling are largely restricted to so-called mechanical recycling, which utilizes melting, granulation and reshaping of discarded polymer products, and feedstock (tertiary) recycling that recovers polymers' building blocks, *e.g*. monomers and oligomers, for reuse.[4] As a rule, properties of the products manufactured from mechanically recycled materials are inferior to those of the goods produced from pristine polymers.[5] On the contrary, chemical tertiary recycling produces pure monomers and oligomers that are suitable for the preparation of new high-quality products. Unfortunately, tertiary recycling is often technologically complex and involves hazardous chemicals (solvents) or harsh conditions (pyrolysis), which make these processes energy demanding and costly. Therefore, the development of efficient polymer re-processing techniques supporting the circular economy would represent a major scientific and technological breakthrough.[6]

The overwhelming majority of synthetic polymers are synthesized by exothermic reactions that cause an ordering of small monomeric building blocks into long-chain macromolecules, which are thermodynamically unstable at elevated temperatures exceeding the polymer's effective (ceiling) stability threashold.[7,8] Therefore, thermal degradation of commercial plastics produces multiple decomposition products, including monomers, oligomers and char.[9] For instance, the thermal degradation of the typical addition polymer polystyrene (PS) yields 10 to 20 various small molecules and oligomeric substances.[10] Consequently, the development of effective methods for tertiary recycling of addition polymers represents an outstanding technological challenge.[4]

Here we report on our discovery of an unprecedented partial depolymerization of polystyrene to its monomer, styrene, at room temperature upon mechanical milling, whereby transition metal(s) present in the milling equipment and atmospheric oxygen catalyze the process.

Mechanical shredding, grinding, or milling are indispensable steps in conventional polymer recycling protocols, and reports about mechanical crushing of polymers are abundant in the literature.[11] Also, very recently, mechanochemical hydrolysis with a large excess of sodium hydroxide has been proposed as a possible way to dismantle a *condensation* polymer,

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[a] Ames Laboratory US DOE, 311 Iowa State University, Ames, IA 50011. E-mail: vbalema@ameslab.gov
[b] Department of Materials Science and Engineering, Clemson University, 161 Sirrine Hall, 515 Calhoun Drive, Clemson, SC 29634-0971. E-mail: luzinov@clemson.edu
[c] Departmentof Chemistry, Iowa State University, 1605 Gilman Hall, Ames, IA 50011

Electronic Supplementary Information (ESI) available: Experimental procedures, the characterization of materials. See DOI: 10.1039/x0xx00000x polyethylene terephthalate.[12] At the same time, to the best of our knowledge, the depolymerization of *addition* polymers to monomers at ambient temperature during mechanical processing has never been reported in the literature, while numerous examples of mechanochemical reactions, including the mechanochemical Wittig reaction,[13a] transformations of metal chalcogenides,[13b] mechano-catalysis,[13c,d] solvent-free synthesis of transition metal complexes and metal organic frameworks[13e,f] as well as other transformations[13g] are known.

In our typical experiment, about 1.5 g of a commercial polystyrene (PS-1 in Table 1, Sigma-Aldrich) was ball milled in a Spex 8000 shaker mill using milling sets manufactured from either hardened steel (HS), tungsten carbide (WC), or silicon nitride (SiN). The processing time was kept at 12 hours unless otherwise indicated; ball–to-material weight ratios were between 10:1 and 13:1, and handling of the samples was carried out either in air or under argon. Excessive heat produced by the mill's motor was removed by forced air cooling. Ball milled materials were immediately analyzed using ^{1}H NMR spectroscopy (600 MHz Avance III Bruker Spectrometer; $CDCl_3$ as a solvent). In several cases, ball milled powders were extracted with methanol and generated solutions were investigated using a coupled gas chromatography – mass spectrometry (GC-MS) in an Agilent 7250 GC/Q-TOF (Quadrupole Time-of-Flight) system. Molecular weights (M_n and M_W, Figure S1) of the milled samples were determined using Gel Permeation Chromatography (GPC) Waters Breeze equipment. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) experiments (Figures S2 and S3) were performed in Q-5000 and Auto TGA 2950HR V5.4A as well as DSC 2920 apparatuses manufactured by TA Instruments. Glass transition temperatures of the polymers were determined using DSC measurements on ~5 mg samples under nitrogen (Figure S3 and Table S1). Electron Paramagnetic Resonance (EPR) spectra were obtained in a constant-wave X-band ELEXSYS E580 EPR spectrometer (Bruker Biospin) at room temperature.

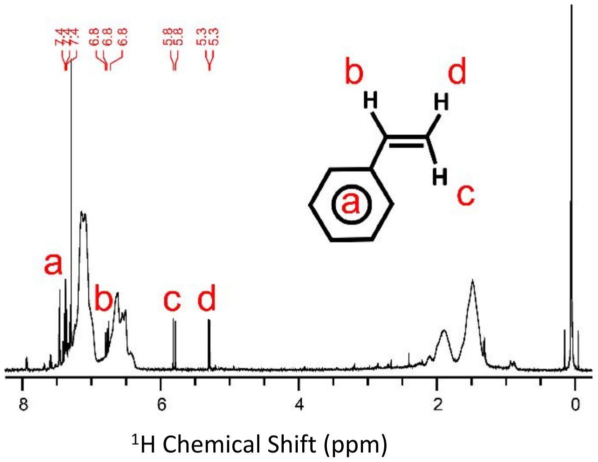

Fig. 1. ^{1}H NMR spectrum of the ball milled commercial polystyrene (PS-2). Solvent: $CDCl_3$; Marked peak positions agree well with those in the spectrum of a commercial styrene shown in Figure S10 and the literature data.[14]

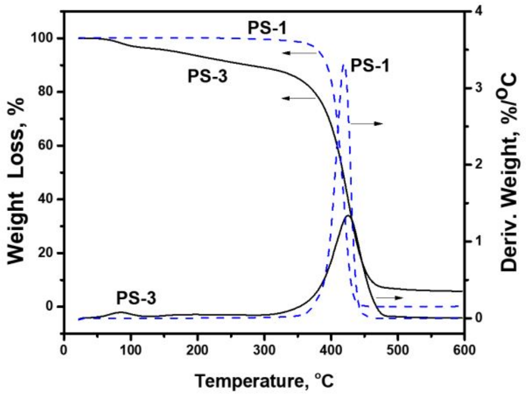

Fig. *2*. TG analysis of commercial (PS-1) and ball milled (PS-3) polystyrene. Thermal decomposition of PS -1 is observed between 350 and 450 °C. In PS-3, the weight loss of ~ 8 wt. % below 170 °C is attributed to the monomeric styrene (b. p. 145 °C).

The ^{1}H NMR spectrum of the pristine polystyrene (PS-1 in Table 1) after its ball milling in a WC milling set in air (PS-2 in Table 1) is shown in Figure 1. Characteristic peaks corresponding to monomeric styrene[14] (δ = 5.2 ppm, d, J = 10.9 Hz; δ = 5.7 ppm, d, J = 17.6 Hz; δ= 6.7 ppm ,dd, J = 17.6 and 10.9 Hz; δ = 7.3 ppm, m, and δ =7.4 ppm, m) are clearly seen in the spectrum, while they are absent in the starting material (Figure S4). A similar result was also obtained for PS-1 ball milled under the same conditions in a HS milling set (PS-3 in Table 1; Figure S5). Comparison of the TGA traces of PS-3 and PS-1 samples reveals the presence of about 8 wt. % of a volatile component in the milled powder, which is absent in the starting polymer (Figure 2). GC-MS analysis of the solution obtained by extracting the as-milled materials with methanol confirmed the presence of the monomeric styrene in the sample (Figure S6); the amount of the monomer detected in the milled material was estimated at about 7 wt. % by GC-MS analysis of the solution containing benzophenone as an internal standard. This amount is consistent with the amount of the volatile material detected by TGA, reflecting the polystyrene conversion during mechanical processing. Contrary to the experiments in air, ball milling of PS-1 in the HS equipment under argon did not produce any substantial quantities of the monomer (PS-4 in Table 1, Figure S7). However, scission and fragmentation of the polymeric chains in the starting material still occurred as follows from the M_n and M_w values shown in Table 1. This indicates that both chain scission and depolymerization processes can start with a hemolytic rupture of C-C bonds in the macromolecule; yet, depending upon the availability of oxygen, independent reaction paths are followed. The EPR spectrum of PS-3 confirmed the formation of stable radical species during the ball milling of polystyrene (Figure 3), even though the milling and all subsequent operations were performed in ambient atmosphere. Two types of radical species can be identified in the EPR spectra of PS-3 samples: oxygen-centered radicals (broad signal centered at a g-value of 2.0733) and carbon-centered radical species (narrow signal centered at a g-value of 2.0026). It is known[15] that polymers such as polyethylene, polypropylene and polymethyl methacrylate can form peroxide radicals under mechanical stress in the presence of oxygen. EPR investigations of polystyrene ball milled[15b] or ground[10e] at the temperature of liquid nitrogen also showed the formation of carbon-centered radicals that were located on the alkene chain, but quickly decayed at room temperature. To the best of our knowledge, the direct detection of carbon-centered free radicals in polymers mechanically processed and handled in air at

Table 1. Polystyrene (PS) ball milled under different processing conditions.

Sample	M_n	M_w	PDI
PS-1: pristine, commercial	87,650	299,235	3.41
PS-2: milled in WC in air	7,683	22,112	2.88
PS-3: milled in HS in air	6,573	14,959	2.28
PS-4: milled in HS in argon	7,628	17,654	2.31
PS-5: H_2O milled in HS in air	6,142	18,927	3.08
PS-6: milled in SiN in air	15,463	25,741	1.66

room temperature has never been reported in the literature. Another interesting observation produced by our study is that ball milling reduces the original molecular weight of PS-1 by factors ranging from 12 to 17 (Table 1). At the same time, the polydispersity indices (PDI) of the polymers in the ball milled samples substantially improve (decrease) as compared to the pristine PS-1. The reduction in PDI indicates uniformity of the macromolecules in processed polymeric materials.[7b]

Hence, longer polymer chains seem to be more susceptible to mechanochemical scission than shorter polymer chain, regardless of the milling atmosphere. Milling PS-1 in the presence of water also causes its fragmentation as indicated by the reduced molecular weight of the PS-5 sample shown in Table 1. At the same time, the depolymerization reaction is suppressed by H_2O, so that the monomeric styrene is absent among the reaction products. The mechanochemical depolymerization of PS-1 is also suppressed when it is performed in a transition metal free (SiN) equipment in air (PS-6 in Table 1, Figure S8). Milling in SiN equipment generates a polymer with reduced M_w, M_n and PDI values, whereby its PDI is the lowest amongst all studied samples, which suggests that the simultaneous presence of both air and a transition metal, i.e. Fe or W, is probably essential for the mechanochemically driven depolymerization process.

At early stages of mechanochemical research, observed chemical transformations were attributed to local temperature increase in solids during ball milling.[16] However, it was later demonstrated[17] that the temperature in the bulk of non-metallic (soft) materials during their milling at room temperature does not normally exceed 60-65 °C. To confirm that the thermal decomposition is not responsible for the mechanochemical depolymerization of polystyrene, a sample consisting of 33 wt. % of ammonium carbonate, $(NH_4)_2CO_3$, and 67 wt. % of PS-1 was ball milled in the HS milling set for 12 hours at room temperature in air. The size and number of balls used in this experiment was identical to those in the experiments that did not involve $(NH_4)_2CO_3$. The irreversible thermal decomposition of $(NH_4)_2CO_3$ into ammonia, carbon dioxide, and water is usually observed at about 60 °C and above,[18] which is far below the decomposition temperature of polystyrene in air (325 °C[19]). TGA of the ball milled material (Figure S9) reveals ~ 10 % weight loss in the sample at about 58 °C, thus suggesting the presence of thermolabile component(s) in the powder even after 12 hours of milling. The limited stability of $(NH_4)_2CO_3$ at room temperature and the formation of water among its decomposition products explains its reduced content in the sample at the time of the TGA measurement as well as the absence of styrene in the milled powder. At the same time, it is quite obvious that the temperature in the bulk of the sample during milling did not exceed 60 °C, which is in line with previous reports.[17]

Apparently, transition metals, *e.g.* iron and tungsten, present as components of the milling equipment, and the oxygen of air act in concert in the mechanochemical depolymerization of PS, as demonstrated above. Furthermore, the inhibiting effect of water on the depolymerization process suggests that it may react with intermediate water-sensitive species or free radical species and deactivate them. These observations allowed us to propose a plausible depolymerization mechanism (Figure 4), which starts with mechanochemical scission of macromolecules in PS and generates carbon-centered free radical species. Once formed, free radicals can react with atmospheric oxygen and produce peroxide intermediates which, in turn, can interact with metallic surfaces of the milling equipment, or metal particles that usually form during milling, and can act as catalysts.[20]

In conclusion, the mechanical milling of polystyrene in a metal-based processing equipment at room temperature in ambient atmosphere facilitates mechanochemical depolymerization of the addition polymer, polystyrene. The depolymerization is accompanied by scission of its macromolecular chains, and can serve as a foundation for the development of novel polymer recycling technologies. It appears that the observed phenomenon is a result of a series of chemical events involving mechanochemical generation of free radicals, oxidation of the latter by ambient oxygen, and subsequent metal-catalyzed release of the monomers. The proposed reaction mechanism is still quite hypothetical and is being investigated in detail that will be reported elsewhere when ready.

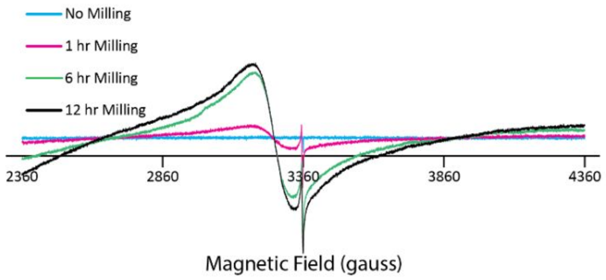

Fig. 3. EPR spectra of PS sample after ball milling (PS-3) in air. Spectra of the starting PS and milled samples are colour coded as shown in the image; samples were handled in air.

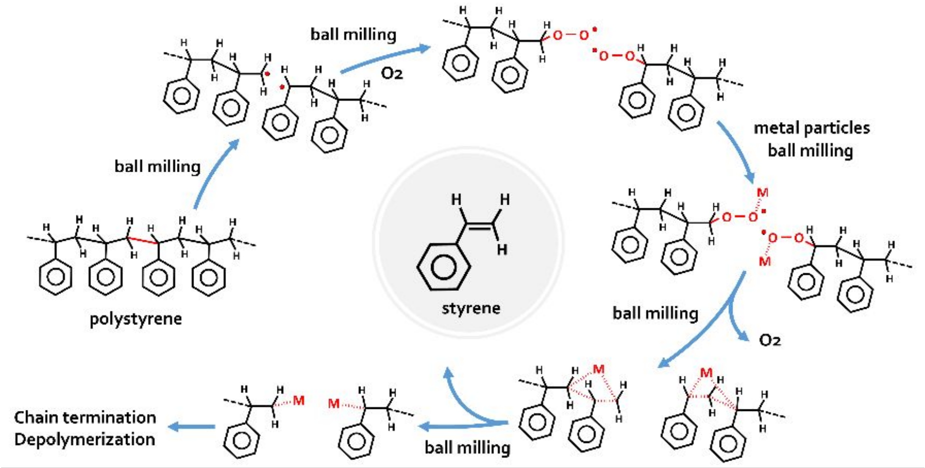

Fig. 4. Proposed mechanism of the mechanochemical depolymerization of polystyrene in metal-containing equipment in the presence of air.

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Conflicts of interest

There are no conflicts to declare

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