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Iron-free mechanochemical limonene inverse vulcanization†

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An iron-free mechanochemical-assisted limonene inverse vulcanization is reported. The process makes use of only limonene and sulphur, industrial waste by-products, under mild conditions (*ca.* 40 °C) and short time (2 h) using a zirconium oxide reactor and a planetary ball mil. The obtained high value products are light yellow solids, readily soluble in chloroform, optically active oligosulfides, which are different from polysulfides reported under conventional conditions (*ca.* 185 °C), as confirmed by NMR spectroscopy and mass spectrometry. A general reaction mechanism is proposed, initiated by homolytic sulphur ring opening triggered by mechanical stress, and involving thiirane intermediates, *via* an addition–elimination reaction of sulphur to the limonene double bonds.

The valorisation of industrial waste by-products is of enormous importance since impacts on both sustainability and circular economy. From this perspective, the development of new products from residues, especially with high added value, is not only challenging but economically attractive. Sulphur has been known since antiquity and is an unwanted by-product of the petrochemical industry, with a worldwide production estimated in 78 million tonnes in 2020.[1] Similarly, limonene is a well-known cyclic monoterpene that is obtained as a by-product from the citrus juice industry, by cold pressing or distillation from orange and lemon fruit peel, reaching a production around 60 thousand tonnes per year.[2] The preparation of polysulfides by inverse vulcanization, a process were elemental sulphur (S_8) is a comonomer and reaction medium, has been explored in the last decades.[3] Applications of these polysulfides have been focused on the development of repairable materials, energy generation and storage, optical devices, and environmental remediation.[3,4] Recently, advances in catalytic inverse vulcanization reactions enabled the use of a wide range of crosslinkers, thus reducing reaction time and temperature, also preventing harmful H_2S production.[5] Very recently, a mechanochemical synthesis of inverse vulcanized polymers was reported using a stainless steel vibratory mill, where different co-polymers where prepared, starting from synthetic and renewable monomers, and aromatic and aliphatic crosslinkers.[6]

Herein, we show the potential of mechanochemistry to perform limonene inverse vulcanization under iron-free conditions at very "low temperatures". In this work (*R*)-limonene was studied as a model olefin for the preparation of high value oligosulfides. The reaction proceeds without heating (*ca.* 40 °C, temperature reached inside the zirconium oxide reactor during the milling process using a planetary ball mil) under solventless conditions. We studied the progress of the reaction over time, at 500 rpm, up to 2 hours. In this time frame, we found that (*R*)-limonene is fully consumed. To find the optimal milling conditions the progress of the reaction was followed by ^{1}H-NMR over time, and information about (*R*)-limonene consumption was achieved by stopping the milling in fixed time intervals. After milling, the obtained crude mixture (light yellow paste) was removed from the reactor (and balls) by washings with chloroform and filtered. The chloroform fraction, after evaporation, led to a yellow solid. The remaining solid obtained in the filtration (chloroform insoluble fraction) was found to be highly soluble in carbon disulfide (CS_2). Attempts to trace a ^{1}H-NMR spectrum using a $CDCl_3/CS_2$ mixture failed since the sample precipitated even with a small amount of $CDCl_3$ (10% v/v), thus precluding full characterization, nevertheless the ^{1}H-NMR using $CDCl_3/CS_2$ 1 : 1 did not show any signal. Fig. 1 shows the ^{1}H-NMR spectrum of the chloroform fraction acquired in $CDCl_3/CS_2$ 9 : 1. The addition of a small amount of CS_2 (10% v/v) allowed the full solubilization of the solid in $CDCl_3$, in which, unexpectedly, the oligosulfides are insoluble. CS_2 was chosen as the NMR co-solvent since does not affect

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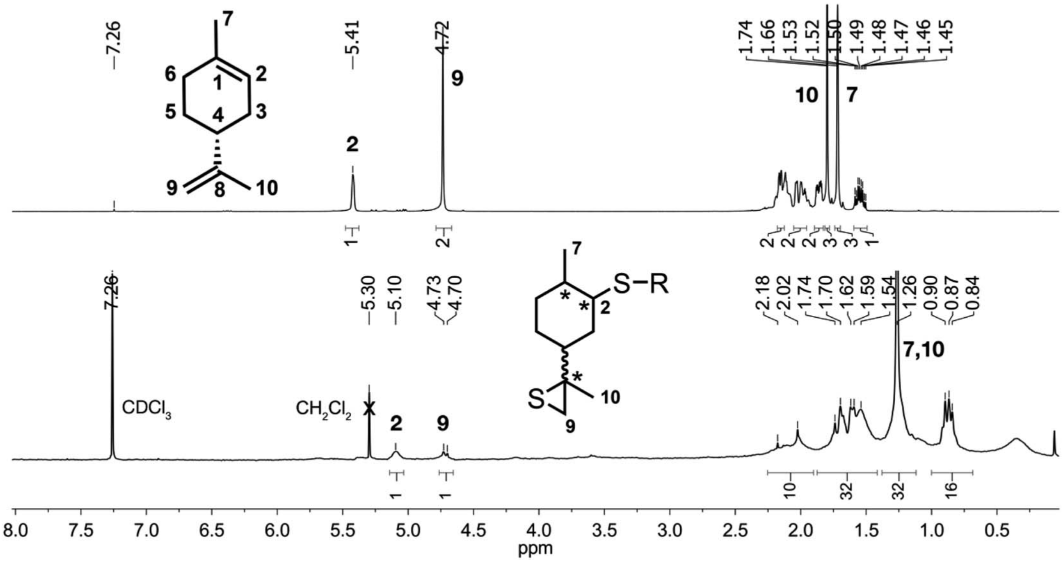


Fig. 1 Limonene mechanochemical inverse vulcanization. ^{1}H-NMR spectrum of limonene in CDCl$_3$ (top) and limonene oligosulfides in CDCl$_3$/CS$_2$ 9 : 1 (bottom).

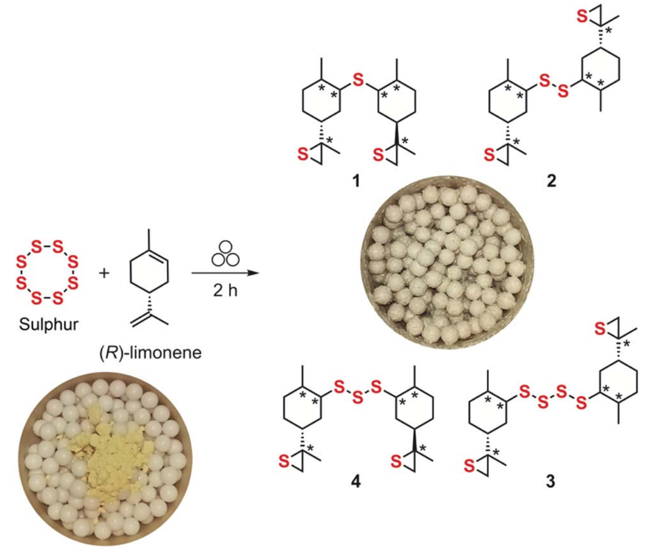
chemical shifts[7] and is a good solvent for S$_8$, which allowed purity control.

The ^{1}H-NMR spectrum does not show the characteristic signals of (*R*)-limonene protons from endocyclic (1H, 5.41 ppm) and exocyclic (2H, 4.72 ppm) double bonds. In this region, the presence of three residual signals may be attributed to (*R*)-limonene thiirane (5.10 ppm, endocyclic proton, H$_2$) and a (*R*)-limonene dimer (4.73 and 4.70 ppm, exocyclic protons, H$_9$), both identified in the mass spectra. The endocyclic proton of (*R*)-limonene thiirane is slightly downshifted ($\Delta H_2 = 0.27$ ppm) to the reported racemate value, the only reference available for these family of compounds (5.37 ppm,[8] 8,9-epithio-1-*p*-menth-1-ene). In analogy, different H$_2$ chemical shifts were found for (*R*)-limonene oxide pure stereoisomers (5.36 (ref. 9) or 5.40 (ref. 10) ppm for (4*R*,8*S*)-8,9-epoxy-*p*-menth-1-ene; 5.38 (ref. 9 and 10) ppm for (4*R*,8*R*)-8,9-epoxy-*p*-menth-1-ene) and the racemic mixture (5.37 (ref. 11) ppm for 8,9-epoxy-*p*-menth-1-ene), which could explain the observed chemical shift.

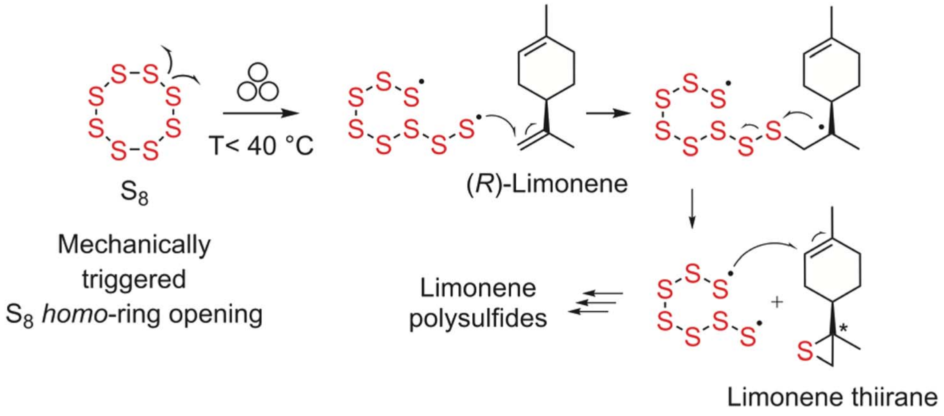
The reaction products were also identified by mass spectrometry, following an optimized protocol using silver(I) infused samples.[12] The mass spectra were acquired in the positive mode, as reported, which allowed us to identify the products formed in the mechanochemical inverse vulcanization (Scheme 1).

We also acquired the spectra in the negative mode, but only the peaks from AgNO$_3$ clusters were observed, with the same pattern of the control injection (AgNO$_3$ and solvents mixture). The spectra acquired in the negative mode, showing the peaks corresponding to AgNO$_3$ ($m/z = 230.9$, 100.0%; 232.9, 94.5%, duplet), and the corresponding dimer ($m/z = 399.7$, 55.1%; 401.6, 100%; 403.6, 47.5%, triplet) and trimer ($m/z = 568.4$, 34.6%; 570.4, 100%; 572.3, 92.9%; 574.3, 30.5%, quartet) clusters were useful in the interpretation of the species observed in the positive mode spectra (see Fig. S2–S4 in the ESI†). Multiple Ag$^+$ ion complexation with sulphur atoms leads to characteristic mass patterns, correlated with the silver isotopic abundance. As in the case of inverse vulcanization by a conventional route (solventless heating),[13] only low molecular weight limonene oligosulfides were found. However, mechanochemical inverse vulcanization leads to the formation of different oligosulfides.

One interesting and rather unusual feature of our methodology using a zirconium oxide reactor and a planetary ball mill, is that, beyond the expected oligosulfides, thiiranes are also formed. The reaction must occur by a catalyst-free sulphur insertion into the limonene double bonds. The homo-ROP of S$_8$



Scheme 1 Mechanosynthesis of (*R*)-limonene oligosulfides. The picture shows the top view of the zirconium oxide reactor and balls before (only visible the yellow sulphur powder) and after (light yellow paste) the reaction.



Scheme 2 Proposed mechanism for the mechanosynthesis of limonene polysulfides using elemental sulphur as the sulphur donor.

has been explored in the preparation of different sulphur copolymers,[14] and is based on the formation of sulphur diradicals upon melting. For the preparation of stable copolymers, avoiding reversible depolymerization, reactions are performed at high temperatures (*ca.* 185 °C), and a yellow to red (or even black) colour change is usually observed. This colour changes

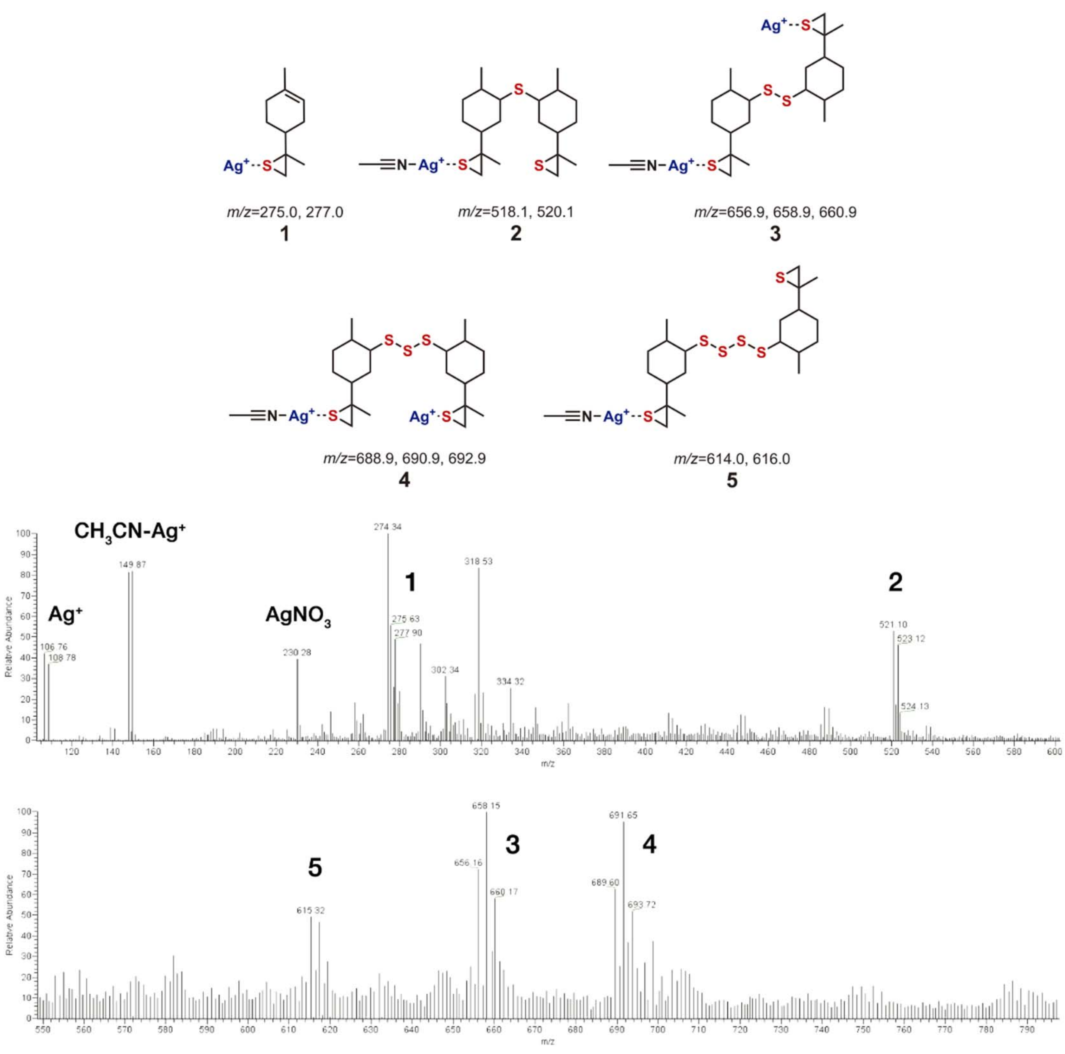


Fig. 2 Identification of limonene inverse vulcanization products obtained by mechanosynthesis. The assignment of $[M + Ag_n]^+$ adducts is shown in the mass spectra.

have been thoroughly investigated, and associated with the monomer ability to form terminal structures by chain transfer, especially the ones containing aromatic or aliphatic terminal olefins, where aliphatic internal olefins (as in the case of limonene) are less prone to the formation of coloured by-products.[15]

In the previously reported[6] mechanochemical synthesis of inverse vulcanized polymers, the use of a zirconium oxide reactor was also investigated in control experiments using monomers 1,3-diisopropenylbenzene (DIB) and styrene. In this case lighter coloured products are obtained, with no remaining sulphur, but found to be insoluble in THF and chloroform, precluding full characterization. However, as we demonstrate in this work, an iron catalysis may be discarded, being mechanical energy a key driving force in this type of reactions.

More recently, a "low temperature" inverse vulcanization (110 °C, below the sulphur melting point) was achieved by the addition of sodium diethyldithiocarbamate trihydrate as a catalyst.[16] Nevertheless, under these harsh conditions, and depending on the co-monomers, side reactions are always observed. In the case of limonene, the aromatization to *p*-cymene is observed.[13] Herein, we used a zirconium oxide reactor and a short reaction time (2 h), being the reaction temperature lower than 30 °C. Under these mild conditions, a decolourization of the initial yellow mixture is observed, and no aromatic signals are detected in the NMR spectra, thus precluding further limonene oxidation.

Thiiranes are important heterocycles, and many synthetic methods have been developed in the last decades.[17,18] To the best of our knowledge, this is the first report of thiiranes mechanosynthesis, under mild catalyst-free conditions and using elemental sulphur as the sulphur donor. Only a few examples of thiirane synthesis are reported using elemental sulphur as the sulphur source, some proceeding with high stereoselectivity,[19,20] not investigated in this work.

The obtained oligosulfides are optically active, with $[\alpha]_D^{20} = -64.4$ ($c = 1.0$, $CHCl_3$), a value that is close to the one found for polysulfides obtained by a conventional route, $[\alpha]_D^{20} = -27.3$ ($c = 1.0$, $CHCl_3$).

We believe that the reaction may follow a radical mechanism, involving an addition–elimination reaction of sulphur to the limonene double bonds (Scheme 2). The homolytic S_8 ring opening may be triggered by mechanical stress, as in the case of ultrasound induced disulfide metathesis.[21]

In the mass spectrum we can also observe a region ($m/z = 200$–400) with a cluster of peaks corresponding to molecules or fragments without sulphur incorporation (absence of the Ag^+ isotopic signature). The peak with the highest intensity, with $m/z = 274.34$, was attributed to a limonene dimer ($m/z = 274.27$), formed *via* a C2–C2′ coupling. The dimerization of limonene is reported to occur in high yield and short reaction time under acid catalytic conditions in refluxing conditions (85%, 2 h, Nafion SAC-13).[22]

Limonene thiiranes and oligosulfides were identified by the $[M + Ag_n]^+$ peaks found in the mass spectra obtained using the positive mode. In the case of polysulfides the silver ions were found to form adducts with acetonitrile (Fig. 2). These adducts were also present in the injection control using the positive mode (see Fig. S2 in the ESI†).

In summary, we demonstrate that mechanosynthesis using zirconium oxide reactors may be explored as a valuable methodology to produce high value products from abundant raw materials such as sulphur and limonene. Also, the milder mechanically triggered reactions originate new products, which are not described by mechanochemical inverse vulcanization using stainless steel reactors or detected under conventional high temperature reactions. Our data highlight the importance of the reactor material, as a key factor to enlarge the scope of mechanically driven synthesis.

Conflicts of interest

There are no conflits to declare.

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