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The use of elemental sulfur as an alternative feedstock for polymeric materials

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An excess of elemental sulfur is generated annually from hydrodesulfurization in petroleum refining processes; however, it has a limited number of uses, of which one example is the production of sulfuric acid. Despite this excess, the development of synthetic and processing methods to convert elemental sulfur into useful chemical substances has not been investigated widely. Here we report a facile method (termed 'inverse vulcanization') to prepare chemically stable and processable polymeric materials through the direct copolymerization of elemental sulfur with vinylic monomers. This methodology enabled the modification of sulfur into processable copolymer forms with tunable thermomechanical properties, which leads to well-defined sulfur-rich micropatterned films created by imprint lithography. We also demonstrate that these copolymers exhibit comparable electrochemical properties to elemental sulfur and could serve as the active material in Li–S batteries, exhibiting high specific capacity (823 mA h g^{-1} at 100 cycles) and enhanced capacity retention.

The preparation of novel polymers and nanocomposites directly from elemental sulfur offers an intriguing new direction in chemistry, materials science and chemical engineering to create novel materials from an alternative chemical feedstock. More than 60 million tons of elemental sulfur are produced annually, the majority of which are a by-product of the hydrodesulfurization process used to reduce sulfur dioxide emissions from the combustion of fossil fuels in petroleum refining. In particular, the refining of bitumous oil or 'oil sand' reservoirs in regions of Canada requires extensive preprocessing to remove sulfurous substances, such as alkylthiols, and ultimately produces elemental sulfur as a by-product (Fig. 1a)[1–3]. Elemental sulfur is utilized most widely for the production of commodity chemicals, such as sulfuric acid and phosphates for fertilizers. Smaller niche markets for specialty chemicals, notably synthetic rubber (for example, tyres) via vulcanization processes and cosmetics, also utilize elemental sulfur directly[4]. However, these existing applications have a limited demand for sulfur so a huge surplus of elemental sulfur on the order of seven million tons is generated annually, the majority of which is stored in powder form or as solid bricks in massive above-ground deposits (Fig. 1a)[1]. Hence, the sheer abundance of elemental sulfur offers a clear and strong motivation to develop innovative chemistry and processing methods for its utilization as a new feedstock for the synthesis of novel polymeric materials.

Although it is known that sulfur possesses a number of interesting properties, namely high electrochemical capacities[5–16] and high refractive indices[17,18], synthetic and processing methods to prepare well-defined materials with high sulfur content are sorely lacking. Elemental sulfur exhibits limited solubility in the vast majority of organic solvents, with the exception of sparing solubility in aromatic media (for example, toluene), carbon disulfide and certain ionic liquids[19]. It has long been known that under ambient conditions elemental sulfur exists primarily in the form of an eight-membered ring (S_8) that melts into a clear yellow liquid phase at 120–124 °C. Rings with 8–35 sulfur atoms are formed and further heating of the liquid sulfur phase above 159 °C (that is, the floor temperature) results in equilibrium ring-opening polymerization (ROP) of the S_8 monomer into a linear polysulfane with diradical chain ends, which subsequently polymerizes into polymeric sulfur of high molecular weight (Fig. 1b). This diradical form of polymeric sulfur exhibits a deep-red colour and depolymerizes back to the monomeric ring forms (of varying ring size) (Fig. 1c). Polymeric sulfur generated from thermal ROP forms a semicrystalline, intractable solid with poor mechanical properties and is not amenable to melt or solution processing. Stabilization of the diradical polymeric sulfur form of this material can be achieved by quenching of the radical chain ends via copolymerization with dienes, such as dicyclopentadiene, which chemically stabilizes the polymer, but still affords a brittle crystalline material[4]. These stabilized polymeric sulfur materials are also used for rubber vulcanization in tyres, but otherwise have found limited utility.

Copolymerization strategies have been explored to modify the properties of elemental sulfur by incorporation into polymeric materials. The seminal work of Penczek and co-workers demonstrates the ability to copolymerize S_8 anionically with propylene sulfide to prepare linear polysulfides with up to nine S–S bonds[20,21]. Stillo and co-workers examined the free radical

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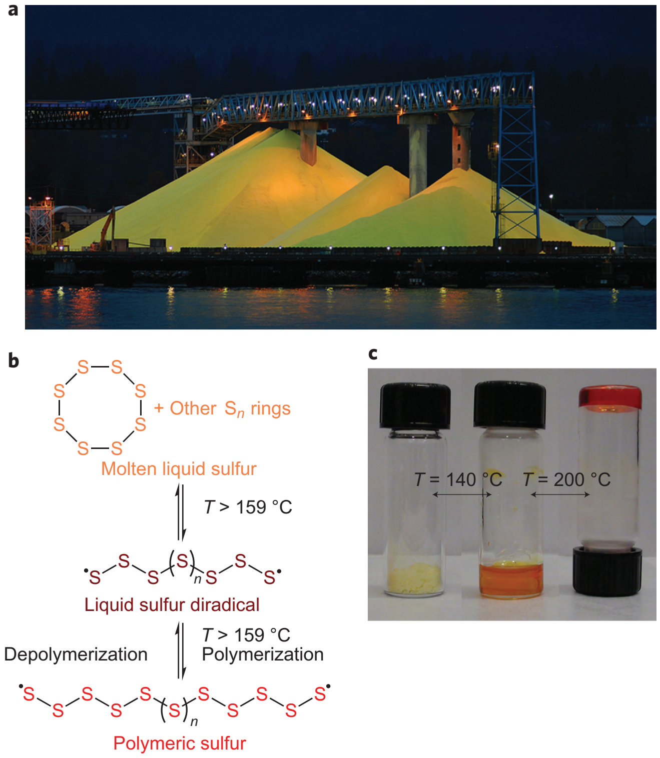

Figure 1 | Elemental sulfur as a feedstock. a, Example of an exposed deposit of elemental sulfur from hydrodesulfurization in petroleum refining processes. The large abundance of sulfur points to an important opportunity to use this as a new chemical feedstock for polymeric materials. **b**, Schematic for thermal ROP of S_8 into polymeric sulfur diradical forms. **c**, Bulk forms of S_8 powder, molten liquid sulfur and polymeric sulfur formed via thermal ROP. Despite the formation of high molecular weight polymeric sulfur from the ROP of S_8, the presence of diradical species results in depolymerization back to monomeric and oligomeric sulfur allotropes.

copolymerization of S_8 with styrene, which afforded mainly oligomeric products, unless divinyl monomers were used to balance the depolymerization process with crosslinking[22]. Tsuda and Takeda reported the copolymerization of diynes with S_8 to form regiorandom polythiophenes[23]. More recently, Ding and Hay demonstrated the copolymerization of cyclic disulfides with S_8, which afforded intractable copolymers with increasing sulfur feed ratios[24]. Although all of these reports point to the potential for sulfur utilization, these materials either have low degrees of sulfur incorporation into the final copolymer or form polymeric materials with limited processability and tunability of properties.

To enable the preparation of chemically stable (that is, suppressed depolymerization) and processable polymers with a very high content of sulfur, we explored the possibility of conducting chemistry directly in molten liquid sulfur as an unconventional medium akin to supercritical fluids and ionic liquids. We demonstrated previously the ability to form gold nanoparticles directly in liquid sulfur from soluble Au(I) complexes, followed by chemical crosslinking to form dispersed, mechanically robust nanocomposites[25]. However, the direct utilization of liquid sulfur as a solventless medium to prepare chemically stable and processable polymeric materials has not been exploited.

Herein, we present the utilization of elemental sulfur for the synthesis of polymeric materials with a very high content of sulfur via inverse vulcanization, which enables the preparation of chemically stable, processable copolymers by copolymerization with divinylic comonomers. In conventional vulcanization, polydienes are crosslinked with a small fraction of sulfur to form synthetic rubber. In the inverse vulcanization process, we describe the stabilization of polymeric sulfur against depolymerization by copolymerizing a large excess of sulfur with a modest amount of small-molecule dienes. Via copolymerization this process enabled, for the first time, the manipulation of elemental sulfur into processable polymeric materials. Additionally, this facile, solvent-free methodology enabled the preparation of multigram-scale copolymers with sulfur that possess tunable thermomechanical properties. As a direct consequence of copolymerizing sulfur with divinylic styrenic comonomers, we were able to prepare soluble prepolymer sulfur resins with a very high content of sulfur (up to 90 wt% sulfur), which could be processed into micropatterned films using polydimethylsiloxane (PDMS) moulds via imprint lithography. With these synthetic developments, we retain many of the desirable properties of elemental sulfur (for example, electrochemical activity), but convert sulfur into a copolymer form with improved chemical and processing characteristics. We demonstrate that this sulfur copolymer can be used as the electroactive material in cathodes for Li–S batteries, which were observed to exhibit the highest-reported specific capacity and energy density to date for a polymeric material.

Results and discussion

The general strategy for inverse vulcanization was the direct dissolution of divinylic monomers into liquid sulfur followed by heating the molten solution above the floor temperature (T_f) for the ROP of S_8, which enabled free-radical copolymerization with 1,3-diisopropenylbenzene (DIB) without the need for additional initiators or organic solvents at 185 °C. Direct control of the thermomechanical properties and optical transparency of poly(sulfur-*random*-1,3-diisopropenylbenzene) (poly(S-*r*-DIB)) materials was achieved by the variation of DIB feed ratios (10–50 wt%) during the S_8 melt copolymerization.

Copolymerization conditions and requirements. For the preparation of poly(S-*r*-DIB) copolymers via inverse vulcanization, the copolymerization of DIB in liquid sulfur was conducted at 185 °C to promote efficient ROP of S_8 and afford chemically stable copolymers that did not readily depolymerize (Fig. 2). Bulk copolymerization in liquid sulfur at 185 °C was conducted to ensure a sufficiently high concentration of sulfur diradicals generated from homolytic cleavage of S_8 to promote the efficient initiation of the polymerization, as well as efficient homopropagation to S_8/sulfur diradicals and cross-propagation to DIB[4]. Copolymerizations were done in liquid sulfur at 185 °C, so comonomers that were both miscible with molten sulfur and nonvolatile were required, which led to the use of DIB. Initial experimental conditions for these reactions explored copolymerizations with relatively DIB-rich feed ratios, S_8 (70 wt%) and DIB (30 wt%), with liquid sulfur heated to 185 °C to cause the onset of ROP. This process was accompanied by a rapid colour change of the medium from yellow to red. At this stage a room-temperature aliquot of DIB was added to the oligomeric sulfur mixture at 185 °C, which, after a very short mixing period, resulted in a homogeneous yellow solution of lowered melt viscosity in comparison to the oligomeric sulfur mixtures. Complete vitrification of the medium was observed within five minutes, at which point the reaction mixture was allowed to cool to room temperature, resulting in the formation of a transparent red polymeric glass. Differential scanning calorimetry (DSC) confirmed that S_8 was fully consumed in the copolymerization, as shown by the absence of two characteristic melting transitions (T_m) from the orthorhombic and monoclinic phases at 109 °C and 119 °C, respectively (see Supplementary Figs S2 and S3 for a discussion of S_8 consumption).

Concomitantly, DSC of the copolymer product revealed the emergence of a new glass transition (T_g) at 17 °C. In contrast to

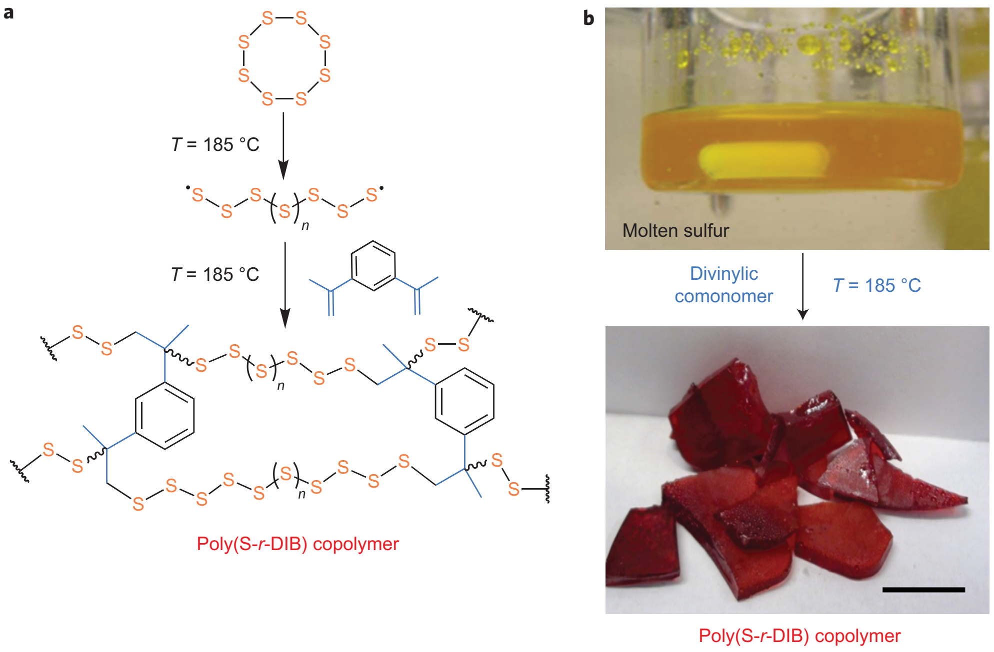

Figure 2 | The copolymerization of S_8 with DIB. a, Synthetic scheme for the copolymerization of S_8 with DIB to form chemically stable sulfur copolymers. **b**, Images of liquid sulfur and poly(S-*r*-DIB) glass with 30 wt% DIB (scale bar, 2 cm). The key feature of this synthetic method is the direct use of liquid sulfur as both the solvent and comonomer, along with DIB, to form chemically stable glassy copolymers.

polymeric sulfur, poly(S-*r*-DIB) glasses were observed to be chemically stable and remained as red transparent films over a period of several months when stored under ambient conditions. A full series of copolymer composition was explored, ranging from 10–50 wt% DIB and 90–50 wt% elemental sulfur, which corresponded, on average, to 44–10 S units per DIB unit in the copolymer, respectively. In general, we observed that all of these feed ratios efficiently copolymerized in bulk at 185 °C, where reaction mixtures with a higher composition of DIB (20–50 wt%) afforded transparent red films; copolymer films with 10 wt% DIB were red and opaque. The origin of the red colour in these copolymers is still under investigation, although similar observations have long been made in the *homo*-ROP of S_8 and remain under speculation[1]. The simplicity of the inverse vulcanization process means that robust large-area films were fabricated easily on a multigram scale by pouring molten solutions of S_8 and DIB prepolymer into petri dishes, or moulds of various shapes, and thermal curing of the resins at 185 °C (Fig. 3a).

In addition to DIB, we found that isocyanate functional α-methylstyrene comonomers can be modified to prepare both mono- or difunctional isopropenyl comonomers that also readily copolymerize with S_8 (see Supplementary Figs S12–S15 for discussion of these new monomers and copolymerization experiments with S_8).

Thermal and rheological properties of sulfur copolymers. Thermal gravimetric analysis and DSC, coupled with rheological characterization of sulfur copolymers, were conducted to investigate the effects of copolymerization on the thermomechanical properties (see Supplementary Figs S17–S23 for details on thermal analysis and rheological characterization). DSC revealed that poly(S-*r*-DIB) copolymers with compositions that ranged from 10 to 50 wt% DIB exhibited T_g values from −14 °C to 28 °C, and increases in DIB content progressively increased T_g of the final copolymer (Fig. 4a). Copolymers with a higher content of DIB (that is, ≥20 wt%) were found to be amorphous, as indicated by the absence of melting/crystallization transitions and from wide-angle X-ray scattering measurements. Poly(S-*r*-DIB) copolymers with a lower content of DIB (10 wt%) exhibited two transitions in DSC that corresponded to a T_g of −14 °C and a weak T_m of 114 °C, which correlated with the optical opacity of films cast from this copolymer. Elemental sulfur exhibits melting transitions at 110 °C and 120 °C in the first scan of DSC, which correspond to melting of orthorhombic and monoclinic phases. Furthermore, polymeric sulfur generated solely by thermal ROP of S_8 exhibited a T_g of −30 °C and complex melting transitions in the range 100–130 °C (ref. 26).

The melt rheology for the poly(S-*r*-DIB) copolymer series, generated from master curves referenced to PDMS standards at 130 °C, indicated that the terminal viscosity progressively increased with higher DIB content for samples that contained 10–30 wt% DIB (Fig. 4b). However, the 50 wt% DIB sample demonstrated a reduction in the terminal viscosity, which is consistent with the formation of highly branched, or ‘hyperbranched’, polymers formed as a result of the higher density of branch points from DIB subunits in the copolymer[27]. Correcting for a change in the glass transition showed that the trend of viscosity with DIB concentration did not change and the 50 wt% sample had the lowest viscosity (see Supplementary Figs S21–23 for rheological characterization of poly(S-*r*-DIB) copolymers).

Structural and kinetic analysis of sulfur copolymers. Although bulk thermal and rheological characterization confirmed the formation of poly(S-*r*-DIB) copolymers, further interrogation of the copolymer structure was necessary. A fundamental challenge encountered in the structural characterization of these materials was the limited solubility of copolymers that contained a high content of S–S repeating units. Fortunately, copolymers with 50 wt% DIB were found to be completely soluble in non-polar organic solvents, which enabled both NMR spectroscopy and size exclusion chromatography (SEC) to be carried out. SEC in tetrahydrofuran of poly(S-*r*-DIB) copolymers with 50 wt% DIB, calibrated against polystyrene standards, exhibited low apparent number-averaged molecular weight and high polydispersity

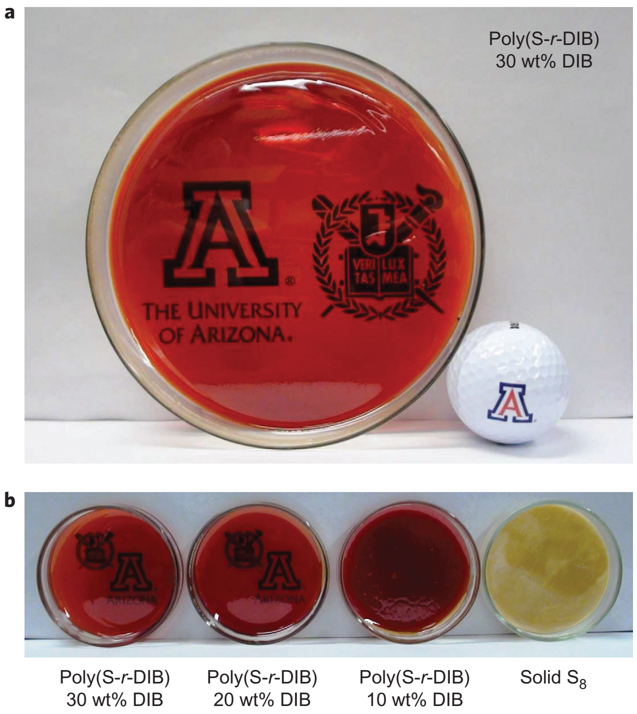

Figure 3 | Transparent glass films of poly(S-*r*-DIB). a, Synthesis on a 25 g scale of poly(S-*r*-DIB) copolymer transparent glass film with 30 wt% DIB cured in a petri dish (outer diameter, 15 cm) with a golf ball as a reference for scale (diameter, 4 cm). **b**, Range of compositions (from the left), 30 wt%, 20 wt%, 10 wt% DIB and elemental sulfur cured in petri dishes (outer diameter, 5 cm). The inverse vulcanization enables facile modification of the composition and properties of poly(S-*r*-DIB) copolymers by controlling the feed ratio of DIB used in the polymerization. The introduction of higher contents of DIB in the final copolymer enabled the fabrication of red transparent bulk films that suppressed the crystallization processes typically observed in bulk forms of S_8.

($M_n = 1{,}260$ g mol^{-1}, $M_w/M_n = 2.70$). The low apparent molar mass and high polydispersity of this copolymer was attributed to both branching through DIB units and predominant termination by intramolecular coupling of sulfur radical branches to form more stable S–S bonded 'loops', which is also a proposed mechanism for suppressed depolymerization as a consequence of DIB copolymerization (see Supplementary Figs S10 and S11 for discussion of structural aspects of poly(S-*r*-DIB) copolymers and the supporting control experiments). Rheological characterization of this copolymer supported this structural hypothesis by the observed zero shear viscosity at the highest DIB content (50 wt%), which suggests that hyperbranched copolymers were formed (Fig. 4b). Further structural characterization of poly(S-*r*-DIB) copolymers using NMR spectroscopy, laser desorption mass spectrometry and SEC were also conducted for structural characterization (see Supplementary Figs S4–S9 for NMR, SEC and mass spectroscopy characterization).

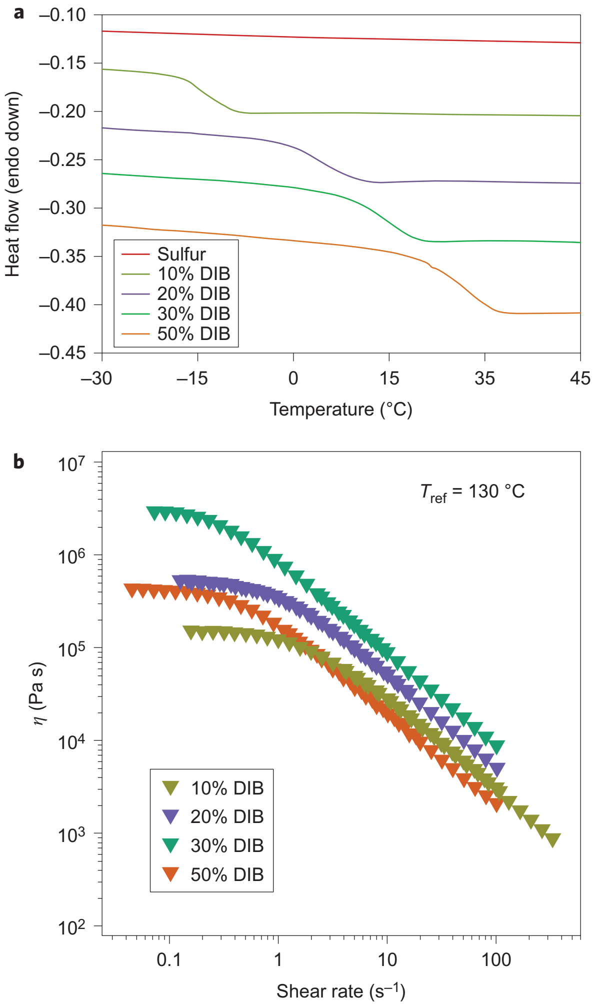

Figure 4 | Thermal and rheological properties of poly(S-*r*-DIB). a, DSC thermograms showing glass transitions (T_g) of elemental sulfur and poly(S-*r*-DIB) of varying DIB content from 10 to 50 wt%. **b**, Zero shear viscosity of poly(S-*r*-DIB) copolymers with varying content of DIB. These measurements demonstrate that control of thermal and rheological properties of these materials can be modulated directly by DIB content in the copolymer.

Melt processing of sulfur copolymers into micropatterned films. As a direct consequence of the inverse vulcanization technique, processable prepolymer forms of elemental sulfur with DIB were prepared, which enabled, for the first time, melt processing of sulfur into patterned films. Imprint lithography[28,29] was utilized to prepare micropatterned poly(S-*r*-DIB) films, for which PDMS moulds were fabricated to generate cylindrical post features that possessed feature sizes and periodicity on the micron scale. Several different PDMS moulds of varying feature size and spatial arrangement were utilized to generate a series of micropatterned films. Micropatterned films of poly(S-*r*-DIB) were prepared by bulk polymerization of S_8 and DIB (30 wt% DIB) held to a low monomer conversion, followed by pouring of the viscous prepolymer into a PDMS mould. Curing at 200 °C for 20 minutes and mould release generated free-standing micropatterned thin films. Scanning electron microscopy (SEM) of moulded poly(S-*r*-DIB) films confirmed a high pattern fidelity and transfer from PDMS masters, with copolymer posts in the range 1–5 μm in height and periodicities in the range 10–20 μm (representative pattern shown in Fig. 5). This particular composition and feed ratio of 70 wt% S_8 and 30 wt% DIB was chosen for moulding primarily for practical reasons associated with favourable viscosity and mixing time required to make and process the sulfur prepolymer before application to the PDMS moulds. Although it would be worthwhile to investigate numerous other processing conditions and methods, we demonstrate here the benefits of inverse vulcanization to modify elemental sulfur into a prepolymer form that exhibits enhanced handling characteristics, which will enable other solution and melt-processing methods to be pursued in future studies.

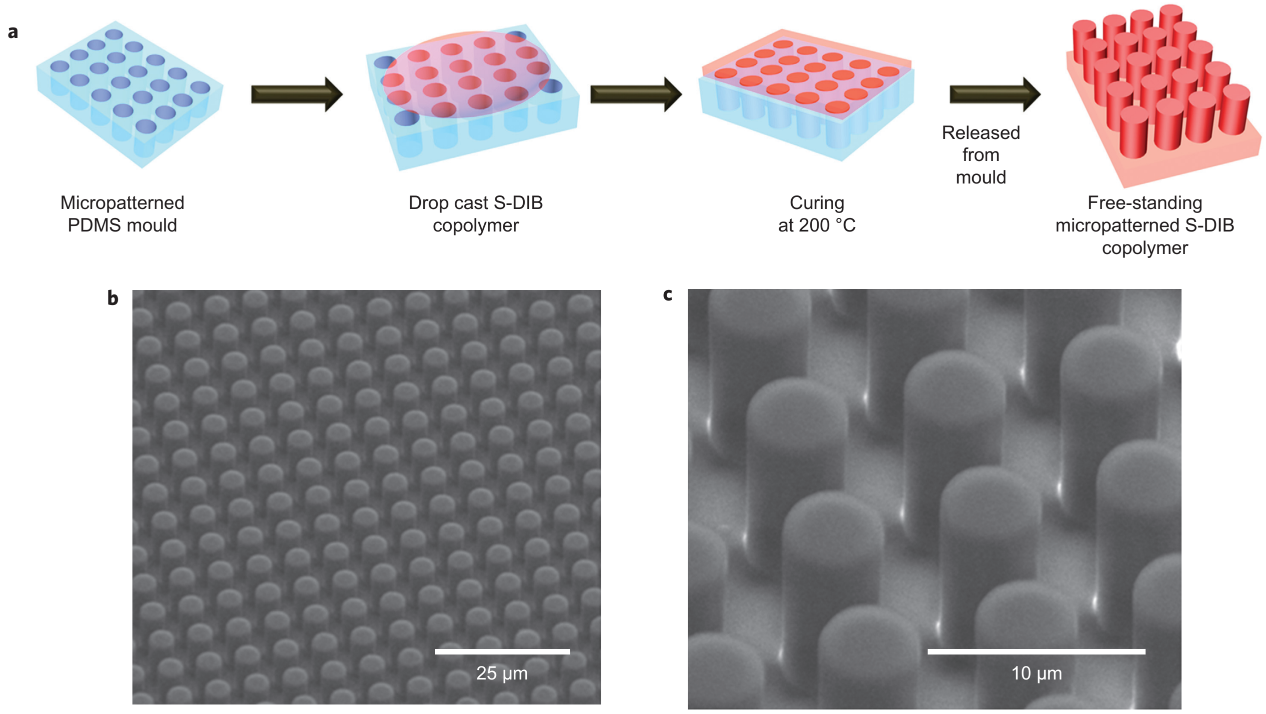

Figure 5 | Imprint lithography of poly(S-*r*-DIB) copolymers to form micropatterned films. **a**, Schematic that depicts imprint lithography of poly(S-*r*-DIB) copolymers in the process used to form the poly(S-*r*-DIB) copolymer micropatterned films, all of which had a composition of 30 wt% DIB and 70 wt% sulfur. **b**,**c**, Environmental SEM of micropatterned poly(S-*r*-DIB) copolymer pillars at different magnifications. Inverse vulcanization enables melt processing of S-DIB resins into PDMS moulds to prepare patterned copolymer films. This marriage of melt processing and imprint lithography with poly(S-*r*-DIB) copolymers allows manipulation into arbitrary shapes and morphologies.

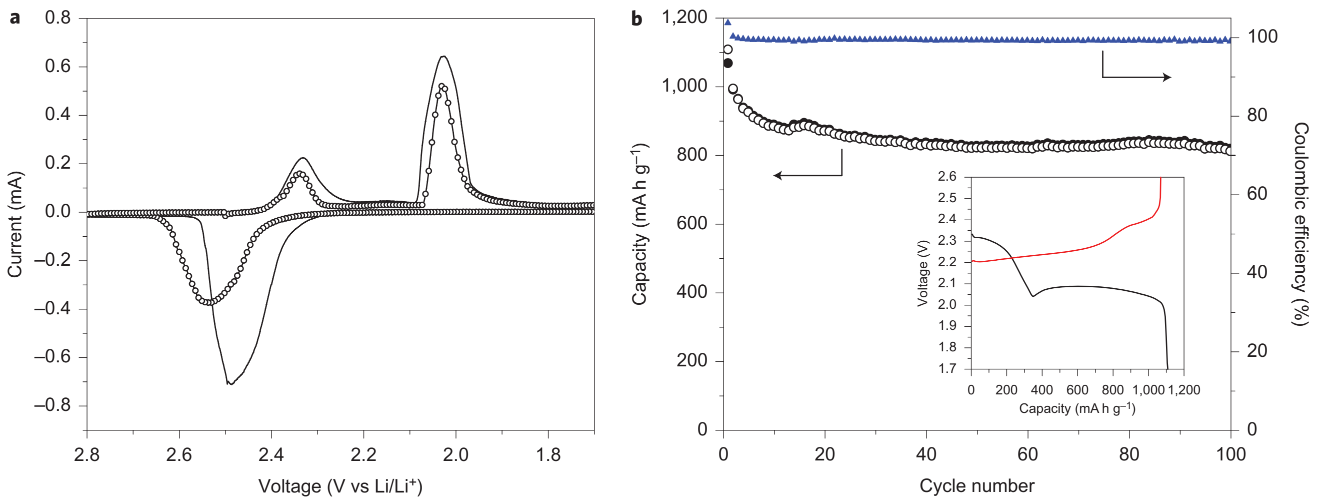

Figure 6 | Electrochemical performance of 10-wt% DIB sulfur copolymer. **a**, CV of pure sulfur (solid black line) and poly(S-*r*-DIB) (10 wt% DIB, open circles) at a scan rate of 20 µV s^{-1}. **b**. Battery cycling data for poly(S-*r*-DIB) (10 wt% DIB, C/10 rate) showing the discharge capacity (open circles), charge capacity (filled circles) and coulombic efficiency (blue triangles) with the inset showing a typical charge/discharge profile. These results show that this composition of poly(S-*r*-DIB) copolymer exhibits comparable voltammetry to that of S_8 and retains high specific capacity when cycled in a Li–S battery.

Electrochemical characterization of copolymers and Li–S battery cathodes. Considerable interest in elemental sulfur and modified sulfur materials has been generated for their use in Li–S batteries. A central motivation of the inverse vulcanization chemistry was to enable modification of elemental sulfur into a processable polymeric form that still retained the electrochemical activity of elemental sulfur. A fundamental challenge in this area is to fabricate sulfur-based cathodes that exhibit retention of high specific capacity after extensive cycling. To interrogate the electrochemical properties of poly(S-*r*-DIB) copolymers, cathodes that incorporated the sulfur copolymer (10 wt% DIB) as the active material were fabricated and electrochemically evaluated by cyclic voltammetry (CV) and battery cycling experiments. The CV results for both S_8 and poly(S-*r*-DIB) were very similar, as shown by peaks at 2.3–2.4 V, which were associated with sulfur reduction generating higher order linear polysulfides, along with a second peak at 2.0–2.1 V assigned to the formation of lower order sulfides down to Li_2S (Fig. 6a). These CV experiments confirmed that poly(S-*r*-DIB) copolymers exhibited very similar electrochemical behaviour to that of S_8. An intriguing feature of these materials was manifested in battery cycling experiments, as the poly(S-*r*-DIB) copolymer exhibited an initial specific discharge capacity of 1,100 mA h g^{-1} with high capacity retention and long-term cycle stability (823 mA h g^{-1} at 100 cycles at a rate of 167.2 mA g^{-1} with respect to sulfur loading, corresponding to C/10 rate). More extensive C-rate studies and experiments above 200 cycles were also conducted, and confirmed the retention of charge capacity over longer cycling periods (see Supplementary Figs S25 and S26 for C-rate studies and extended cycling experiments). Previous reports on enhanced sulfur-based cathodes required the preparation of complex core–shell colloids that encapsulated elemental sulfur with a conductive shell of either a conjugated polymer or a conductive carbon coating[10,13–15]. The specific capacity of Li–S batteries made from these core–shell colloids as the active material ranged from 600 to 1,000 mA h g^{-1} at 100 cycles and comparable C-rates. Although the capacity and cycle stability of poly(S-*r*-DIB)-based cathodes fell within the range achieved using core–shell colloid-derived electrodes, the synthetic simplicity, low cost and amenability to large-scale production of poly(S-*r*-DIB) copolymers are distinctive advantages relative to the core–shell colloid examples previously discussed. Furthermore, these poly(S-*r*-DIB) copolymers exhibit the highest specific capacity of any polymer-based cathode reported to date. Although the cause of these exceptional electrochemical properties is still under investigation, we demonstrate that these inexpensive, easily synthesized sulfur copolymers exhibit enhanced electrochemical properties as a direct consequence of copolymerization from inverse vulcanization.

Conclusions

In conclusion, we demonstrate here the development of a new synthetic methodology, termed inverse vulcanization, that has the ability to use elemental sulfur as a novel feedstock to prepare chemically stable copolymers. As a direct consequence of this copolymerization technique, we prepared copolymers with a very high content of sulfur that were both solution and melt processable, in sharp contrast to the properties of elemental sulfur. Furthermore, we demonstrate that these sulfur copolymers maintain electrochemical activity and are suitable as the active material in Li–S batteries. This general synthetic approach is anticipated to open a new avenue of sulfur utilization research for polymeric materials and enable the preparation of a novel class of electrochemically active materials for battery applications.

Methods

General procedure for the preparation of poly(S-*r*-DIB). To a 24 ml glass vial equipped with a magnetic stir bar was added sulfur and the vial was then heated to 185 °C in a thermostatted oil bath until a clear orange-coloured molten phase was formed. DIB was then added directly to the molten sulfur medium via a syringe. The resulting mixture was stirred at 185 °C for 8–10 minutes, which resulted in vitrification of the reaction medium. The product was then taken directly from the vial using a metal spatula and the magnetic stir bar removed to determine the yields after allowing the reaction mixture to cool to room temperature (detailed synthetic and processing protocols are given in the Supporting Information).

Preparation of micropatterned poly(S-*r*-DIB) copolymers. To a 24 ml glass vial equipped with a magnetic stir bar was added the sulfur (S_8, 3.50 g, 13.7 mmol) and the vial was then heated to 185 °C in a thermostatted oil bath until a clear orange-coloured molten phase was formed. 1,3-DIB (1.50 g, 9.48 mmol) was added to the molten sulfur medium and the resulting mixture was further heated at this temperature for a few minutes to form a viscous red-coloured prepolymer resin. The viscous solution was placed onto a micropatterned PDMS mould and then immediately placed in an oven heated at 200 °C, cured for 30 minutes, cooled to room temperature and removed carefully from the PDMS mould.

Coin-cell fabrication and experimental electrochemical testing. Poly(S-*r*-DIB) (10 wt% DIB) was combined with conductive carbon and polyethylene as a binder in a mass ratio of 75:20:5, respectively, and milled into a slurry with chloroform. The slurry was then blade cast onto carbon-coated aluminium foil and dried in air. This cathode was assembled into CR2032 coin cells with a polypropylene separator and lithium foil as the reference/counter electrode in an argon-filled glove box. The electrolyte used was 0.38 M lithium bis(trifluoromethane)sulfonimide, 0.31 M lithium nitrate in a 1:1 (v/v) mixture of 1,3-dioxolane and 1,2-dimethoxy ethane. CV was done on a CH Instruments 600 potentiostat at a scan rate of 20 $\mu V\ s^{-1}$ from 2.8 to 1.5 V. Battery cycling was done on an Arbin BT2000 battery tester at a rate of C/10 (167 mA g^{-1} sulfur) from 1.7 to 2.6 V.

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Author contributions

W.J.C., J.J.G., E.T.K., H.S.Y., R.S.G., P.T., Y-E.S., K.C. and J.P. developed the concept and conceived the experiments. J.J.G., E.T.K., W.J.C., A.G.S., P.T.D., H.J.J., J.J.P., A.S. and H.S.Y. performed the laboratory experiments and analysed the results. J.J.W., N.A.N., B.W.G. and M.E.M. provided support for polymer characterization. W.J.C., K.C. and J.P. co-wrote the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to Y-E.S., K.C. and J.P.

Competing financial interests

The authors declare no competing financial interests.