



Solvated Inverse vulcanisation by photopolymerisation

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ARTICLE INFO

Keywords:

Sulfur
Polymer
Inverse vulcanisation
Photopolymerisation

ABSTRACT

Inverse Vulcanisation (IV) under neat reaction conditions (without solvent) has enabled the research and development of the fundamental chemistry as well as the generation of unique sulfur-rich polymers with unprecedented properties. However, such bulk polymerisation can be problematic, especially with high molecular weight. The energetics of the thermal polymerisation process, combined with poor heat control of solvent-free polymerisation, cause risks of dangerous auto-acceleration if the process is scaled up. The required high temperatures (>160 °C or 135 °C even with catalysts), exceed the boiling point of most commonplace organic solvents, preventing implementation of solvents for IV under thermal conditions. We report here a photo-induced IV polymerisation in solvent at room temperature. The reactions proceed smoothly and efficiently with excellent yields, despite the potential negative factors of reflection, refraction, and low absorption intensity of light by these organic solvents, opening an attractive avenue for the preparation of functional sulfur-rich polymers as well as their potential applications. The extension of crosslinkers to the value-added C5 fraction of industrial byproduct and β -carotene showcase the benefit of this low temperature protocol. Mechanistic study reveals that the moisture in both substrates and solvents might play a key role for the generation of toxic H₂S by-product in IV reaction under thermal conditions, with photopolymerisation remaining un-affected. This protocol not only extensively expands the scope of crosslinkers for the IV reaction together with resultant polymers, but also provides a potential scale-up route for industrial application by avoiding the generation of toxic H₂S by-product and possible explosion risk with high temperature.

1. Introduction

Notwithstanding environmental, operational, and cost concerns, solvents undoubtedly play a pivotal role in chemistry, especially synthetic chemistry, ranging from the production of small complexes, supramolecular structures, and macromolecules.[1–9] Solvents can even be critical in many cases. [5,7–9] Interestingly, neat reaction conditions, that is reactions proceeding without any solvent involvement, are tentatively preferred for the same reasons, regarding both the chemical and physical properties of the reactants along with reaction

driven-forces. [5] However, many limitations co-occur with neat reaction conditions, typically for those involving all solid-state reactants at low temperature which circumvent the interactions among reactants as well as their diffusion process. Inverse vulcanisation (IV) of elemental sulfur with covalent carbon bonds (alkenes/alkynes) to generate a new family of functional sulfur-rich polymers was originally invented as a neat reaction under thermal conditions. [10–16] Of particular note, the elemental sulfur here acts as both the reactant and solvent at its molten stage upon heating over 120 °C. [10,16] Even still, with this method there is hinderance for the use of solid crosslinkers in IV reaction

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<https://doi.org/10.1016/j.eurpolymj.2024.112815>

Received 16 October 2023; Received in revised form 11 January 2024; Accepted 29 January 2024

Available online 2 February 2024

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(Fig. 1).

Elemental sulfur is produced at nearly 70 million tons annually as by-products from the refining of petroleum and natural gas. The sulfur supply outweighs demand, making many sulfur stocks unwanted, abundant, cheap, and environmental problematic. [12,15,17,18] Since the pioneering report by Pyun and coworkers in 2013, [16] IV with elemental sulfur has received much interest, elevating both the fundamental chemistry and versatile applications of sulfur-rich polymers. [94] Many developments have been achieved, including broadening of crosslinker scope, [19–36] development of synthetic methods, [26,28,30,31,37–49] optimization of reaction conditions, [37,38,40] characterization of both chemical and physical properties, [19,20,23,50–62] and various applications from their unique functionalities. [20,22,24,34,48,51,56,63–71] However, a significant challenge remains regarding the harsh thermal conditions applied which generally lead to: i) the constraining of the scope of crosslinkers; ii) production of toxic H₂S by-products; iii) uncertainty of properties for obtained polymers; iv) and danger of auto-acceleration or even explosion of the polymerisation. [10,61,68,72] Realizing the unmet need for tackling those challenges of harsh thermal reaction conditions, we sought to investigate mild reaction conditions and simple synthetic methods for IV. Photoinduced IV with elemental sulfur was recently found to be feasible for a broad scope of crosslinkers/comonomers at room temperature with specific wavelengths of light irradiation. [73] The significant advances of this photoinduced IV include: i) very mild conditions of ambient temperature; ii) volatile and gaseous alkenes/alkynes as crosslinkers introduced to IV for the first time and the latter are easily available coupled with scale-up capability; iii) preventing toxic H₂S by-product generation; iv) avoidance of energy-intensive curing processes that are common in thermal IV; v) near quantitative yields; vi) potential for more sustainable alternatives for environmentally harmful commodity plastics to be generated by sulfur-rich polymers with the same gaseous comonomers, e.g. Poly(S-EE) vs polyethylene, Poly(S-PE) vs polypropene, Poly(S-VC) vs polyvinyl chloride.

However, photo-induced IV was demonstrated predominantly for neat reaction conditions, albeit at room temperature. It is worth noting that a tiny amount of solvent (~20 μ L) is essential for the photo-induced IV with gaseous crosslinkers/comonomers to occur and proceed,

presumably facilitating the diffusion process of gas molecules into the surface of elemental sulfur. This finding inspired us to further investigate the exploitation and potential benefit of solvents for photo-induced IV with elemental sulfur. Given the high melting and reaction temperature of elemental sulfur, there are few previous reports of IV polymers being directly synthesized in solution [74,75], as these temperatures would be above the boiling point of many common solvents – which would therefore require high pressures and cause safety concerns. Despite the potential negative factors of reflection, refraction, and low absorption intensity of light by organic solvents, IV in solvents by photopolymerisation proceeded smoothly and efficiently with excellent yield, especially to solid crosslinkers, opening an attractive new avenue for assessing the preparation of functional sulfur-rich polymers as well as their potential applications.

2. Results and discussion

2.1. Screening of the reaction conditions

To pinpoint the solvent effect for photo-induced IV at ambient temperature, a series of common organic solvents have been evaluated by using the reaction of diisopropenyl benzene (DIB) with elemental sulfur as a model, with toluene and chloroform being optimal. Given the propensity of inevitable reflection, refraction, and variable absorption intensity of light by solvents, more energetic 380 nm wavelength of UV light, as originated from the photoinduced IV under neat reaction conditions, was conducted for the screening of the reaction conditions initially (Table 1). Moderate to good yields of isolated solids were obtained for the reactions performed in toluene, dichloromethane (DCM), chloroform, xylene, and tetrahydrofuran (THF) with a 1:1 mass ratio of S₈ and DIB at room temperature (19 °C) for 48 h (Entries 1–4, and 6, Table 1). Interestingly, the same reaction went smoothly in blended solvents with reasonable yields (Entries 18–19, Table 1). Further optimizations were carried out with variation of light wavelength and reaction time corresponding to the solvents used (Table 2, and Table S1 and S2), with 365 nm in chloroform being optimal, affording the highest isolated yield of solid material of 87 % (Entry 6, Table 2). It should be noted that yields were recorded as the mass of solid isolated by filtration,

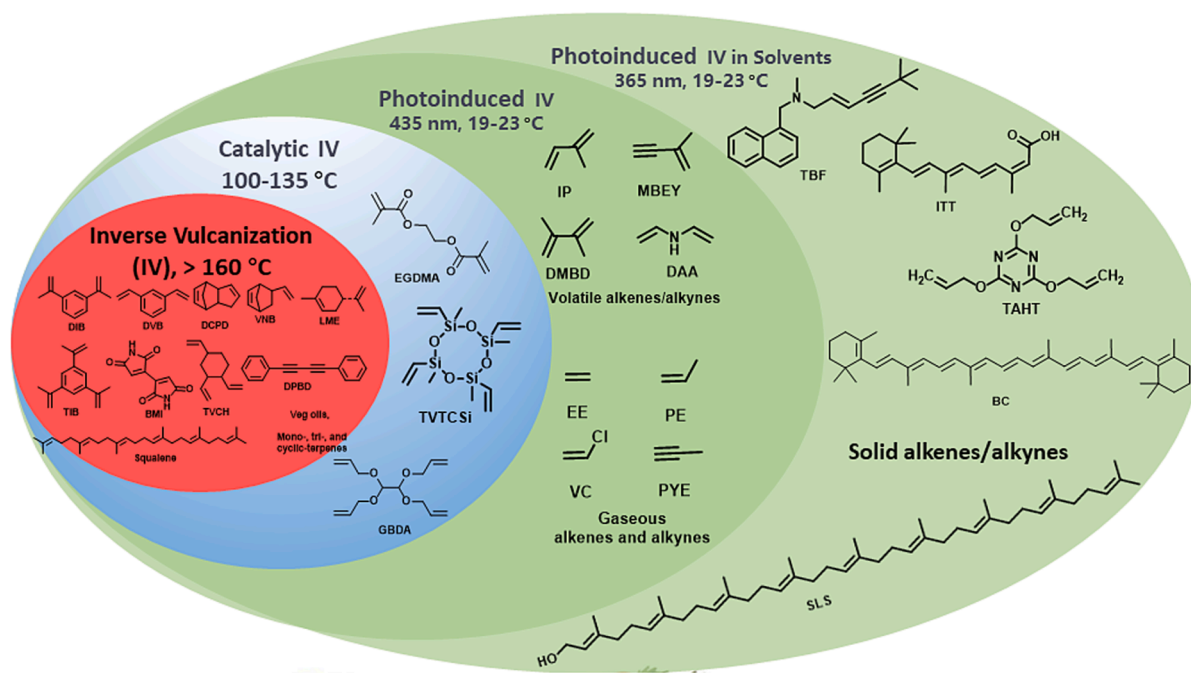


Fig. 1. Representative scope of the crosslinkers for IV polymerisations under different reaction conditions with solid crosslinkers only feasible for photoinduced IV in solvents (Current work).

Table 1

Screening of the solvents for photoinduced IV of S₈ and DIB with 380 nm UV light at room temperature ^a.

Entry	Solvent ^b	Yield (%) ^c	Entry	Solvent ^b	Yield (%) ^c
1	TL	58	11	DME	4
2	DCM	45	12	CP	3
3	CHCl ₃	35	13	CAN	10
4	Xylene	41	14	NMP	ND
5	H ₂ O	25	15	DMF	ND
6	THF	78	16	NPA	ND
7	EA	8	17	DMSO	ND
8	n-hexane	10	18	TL + CHCl ₃	38
9	1,4-dioxane	6	19	TL + DCM	18
10	DCE	6	20 ^d	TL	ND

^a): Reaction conditions: Equal mass of sulfur (50 mg, 0.195 mmol) and DIB (50 mg, 0.31 mmol) were added into a 20 mL photoreaction tube (quartz tube) with solvent (1 mL) at room temperature and the mixture was reacted at room temperature for 48 h with light irradiation (380 nm wavelength).

^b): TL = Toluene; DCM = Dichloromethane; EA = Ethyl Acetate; DCE = dichloroethane; DME = Ethylene glycol dimethyl ether; CP = Acetone; ACN = Acetonitrile; NMP = *N*-methyl pyrrolidone; DMF = *N,N*-Dimethylformamide; NPA = *n*-Propyl Alcohol.

^c): Yield of isolated solids by filtration, ND = Not Detectable;

^d): There is no reaction occurred for the same IV reaction in Toluene in the presence of Zn(DTC)₂ catalyst (5 % mass ratio to S₈) at 110 °C for 15 h, neither at 135 °C for the same reaction time.

Table 2

Further optimization of time, wavelength, and solvents for photoinduced IV of S₈ and DIB with UV light at room temperature.

Entry	Material ratio	Light source (nm)	solvent	Time (h)	T (°C)	Yield (%)
1	1:1	380	TL	24	19	NR
2	1:1	380	TL	36	19	17
3	1:1	380	TL	48	19	58
4	1:1	380	TL	60	19	18
5	1:1	380	TL	72	19	25
6	1:1	365	CHCl ₃	48	19	87
7	1:1	365	MeOH	48	19	67
8	1:1	365	EtOH	48	19	70
9	1:1	365	NPA	48	19	7
10	1:1	365	IPA	48	19	4
11	1:1	365	DMF	48	19	8
12	1:1	365	DMSO	48	19	5
13	1:1	365	NMP	48	19	ND
14	2:3	365	CHCl ₃	48	19	21

as so do not take into account solid unreacted S₈ being isolated with the product, or soluble reaction products passing through the filtration. From the light yellow color of the aqueous and alcohol products (Figures S3 and S4), it is likely they contain unreacted S₈, as well as polymeric products detected by NMR (Figure S5). In the case of high boiling solvents such as DMF, DMSO, and NMP, which showed either no or very little isolated solids, but a distinct colour change in the reaction (see figures S6 and S7), it is likely that while there was reaction between the monomer and the sulfur, the products remained in solution, perhaps because of the activity of these solvents to break S-S bonds, preventing the formation of higher molecular weight polymers, as has been shown previously for DMF. [76].

Of important note is that there are negligible resultant polymers obtained for the same IV reaction under thermal conditions in toluene in the presence of Zn(DTC)₂ (5 % mass ratio to S₈) at either 110 or 135 °C for 15 h (Entry 20, Table 1), echoing a different mechanism operating for IV polymerisations with thermal and light conditions. [73] The resultant sulfur-rich polymers were fully characterized by NMR, DSC, TGA, PXRD, FTIR, and GPC (Figure S8), implicating similar polymers obtained aligning with previous thermal and light-IV reactions under neat conditions.

Key to the solvated IV with light is the optical performance of these solvents when saturated with sulfur, and has consequently been investigated, while the same properties of the pristine solvents were well demonstrated in the literature. [1,77] As shown in Figure S9, the light wavelengths at 360–380 nm are most frequently encountered as high and efficient absorption band for almost all solvents with saturated sulfur screened through the UV full spectrum initially, with dichloromethane, chloroform, toluene, and xylene being distinguished for their good capability of dissolving more elemental sulfur (Table S3, Figure S9). The further detailed full UV spectrum scanning of chloroform, toluene and their sulfur saturated counterparts confirmed the same observation (Figure S10), elevating 365 nm wavelength as the choice for the photoinduced IV polymerisations in solvents. The absorption intensity of light at 365 nm by those solvents and their sulfur saturated counterparts revealed a dramatic increase for the latter with similar refractive index for most of them (Figures S11–S12, Table S4), aligning with the previous results of reaction conditions screened. Chloroform was then chosen as solvent for the exploration of the scope of the solvated IV polymerisation due to its simple and easy removal after reaction together with cost considerations.

2.2. Investigating solid crosslinkers

The solvated IV of photopolymerisation offers significant advantages in cases where it would be used for solid crosslinkers, allowing the production of unique sulfur-rich polymers. A series of solid crosslinkers such as Beta-Carotene (BC), Isotretinoin (ITT), Solanesol (SLS), 1,3,5-Triacryloylhexahydro-1,3,5-triazine (TAHT), and Terbinafine (TBF) were tested for solvated IV with light, affording sulfur-rich polymers confirmed by the full characterizations of ¹H NMR, FTIR, DSC, TGA, PXRD, and EA (Fig. 2; Entries 14–18, Table S5; Figures S13–S14, Figures S17–S21, Figures S34–S39, Figures S48–S52, Figures S65–S69). As demonstrated in Fig. 2b & c, almost complete consumption of C = C double bonds in BC were evidenced by both ¹H NMR and FTIR spectra. Once again amorphous polymers with a faint T_g of –23.4 °C was recorded for the obtained poly(S-BC) (Fig. 2d & e).

2.3. Validating for liquid and gaseous crosslinkers

We subsequently expanded the protocol to crosslinkers and/or monomers reported previously in the literature, [10–16] including alkenes and alkynes in both liquid and gaseous states. All the representative solvated IV polymerisations proceeded smoothly and successfully albeit with slightly different isolated yields, exemplified by common high-boiling point crosslinkers such as dicyclopentadiene (DCPD), myrcene (MYE), 5-vinylbicyclo[2.2.1]hept-2-ene (VNB), phenylacetylene (PA), diallylamine (DAA), low-boiling point agents such as isoprene (IP), 2-methyl-1-butyl-3-yne (MBEY), as well as gaseous monomers such as ethylene (EE), propene (PE), propyne (PYE) and vinyl chloride (VC) (Table S6). All the resultant sulfur-rich polymers are stable at ambient temperature and have been fully characterized by ¹H NMR, FT-IR, DSC, TGA, PXRD, EA, etc. with comparable data and results to those reported previously under both thermal and light conditions as illustrated in the supplementary information (Figures S17–S83). Of particular note is that the C5 fraction, by-products of the ethylene production process, [78–81] which contains several high value-added components, such as isoprene (IP), piperylene (PD), cyclopentadiene (CPD) etc. is feasible by this protocol. In contrast to the exact structural reactant requirement necessitated for many organic reactions, [82–85] the solution photo-induced IV reaction seems tolerant of these structural variations. Although extracting high value-added diolefins in the cracked C5 fraction by separation technology is an effective method to improve the value of resource utilization together with the production of special rubber, petroleum resins, pesticides, fragrances, curing agents, flame retardants, pharmaceuticals, and other petrochemicals and/or fine chemical products from these obtained diolefins, [78–81]

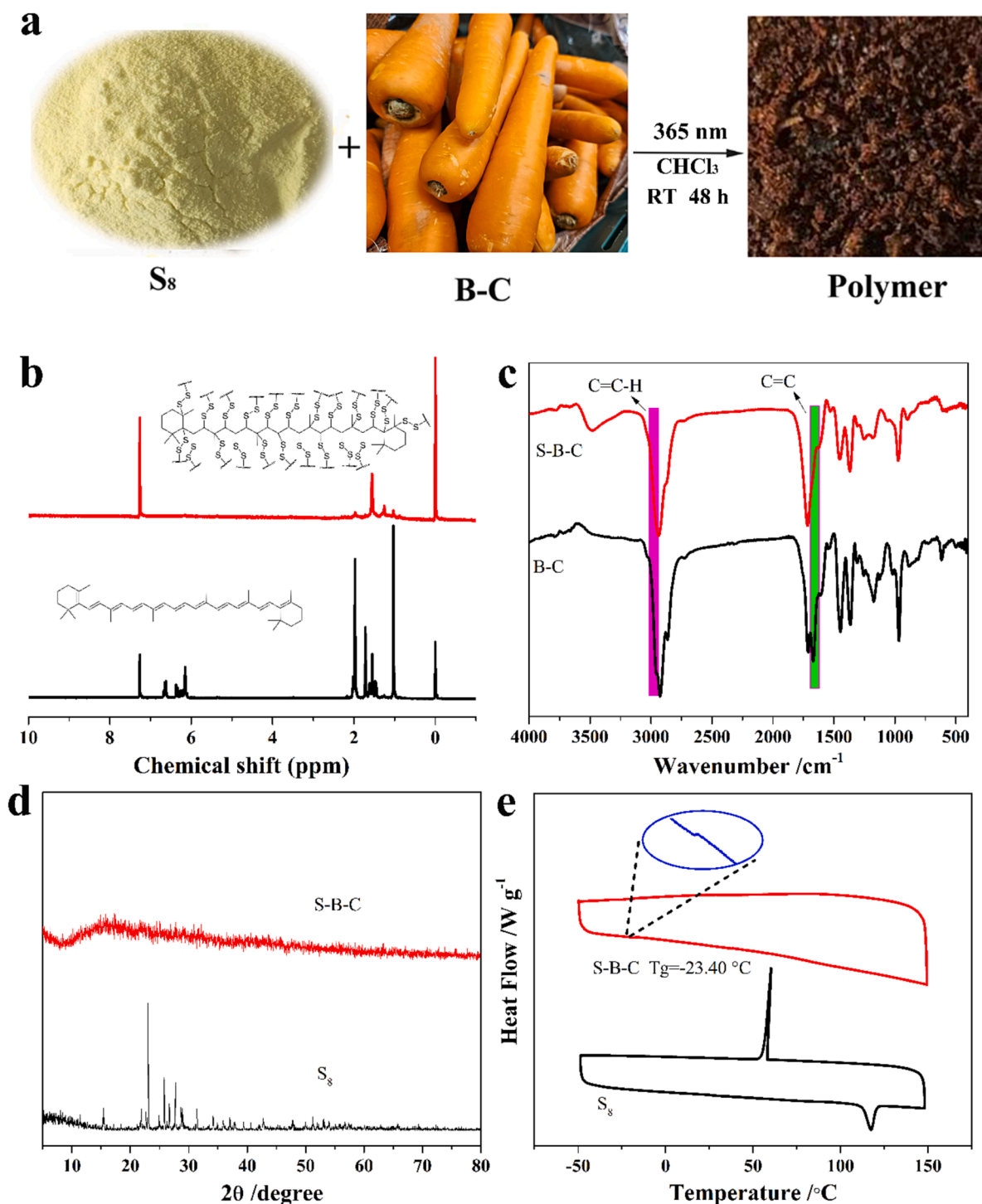


Fig. 2. Representative of solvated IV with solid crosslinkers. a) Solvated IV between S_8 and BC in chloroform with 365 nm light for 48 h at room temperature; b) ^1H NMR of BC (bottom) and poly (S-BC) (top); c) FTIR of BC (bottom) and poly(S-BC) (top); d) PXRD of S_8 (bottom) and poly(S-BC) (top); e) DSC of S_8 (bottom) and poly (S-BC) (top).

functional materials prepared with unseparated C5 as raw material are scarce. Unique sulfur-rich organic polymers with this abundant resource were developed, occurring at different ratios. Presumably, it due to the multi components of C5 with their unsaturated carbon bonds, characterised by ^1H NMR, FTIR, DSC, TGA, PXRD, and EA with exemplified resultant polymers of S-C5 (1:1) and S-C5 (2:1) (Figures S82-S83). The exploration of properties and the potential applications of these resultant polymers with C5 such as insulation, cathode materials for lithium-sulfur batteries, optical lenses, and others, are ongoing.

Scale-up of solvated IV with solid crosslinkers was found to be feasible as exemplified with BC. Thus, 2 g of a mixture of S_8 and BC successfully converted into the desired polymers by using 365 nm light irradiation at room temperature with 93 % isolated yield as revealed by DSC, TGA, and PXRD, so were the poly(S-PA) (Figures S84-S87).

The absorption of metal ions by the resultant polymers from solvated IV was attempted by the consumption of Cu^{2+} and Cr^{6+} in solution. As shown in Figures S84a, all the resultant polymers from solvated IV with solid crosslinkers, including poly(S-TBF), poly(S-BC), poly(S-ITT), and

poly(S-SLS) possessed excellent adsorption ability for concentrations of Cu^{2+} of 1.4 mg/L at room temperature, approaching 85 % – 92 % removal rate; whilst a predilection of Cr^{6+} with high concentrations of 1.4 mg/L by specific poly(S-TBF) was observed, with low to moderate removal rate for the rest of poly(S-BC), poly(S-ITT), and poly(S-SLS) (95 % vs 9–37 %, Figure S88b). Poly(S-IP) was found to be feasible for the absorption of organic molecules, organic dye Rhodamine B, with saturated absorption capability reaching at the first 40 min (Figure S85).

Taking the privileged advantages of solvated IV with light, a specific constructed solid crosslinker was designed and synthesized for its unique functionality and applications as anti-bacterial materials. Although the antibacterial property and applications of the sulfur-rich polymers resulted from IV has been demonstrated by several samples in the literature as orientated from antibacterial ability of sulfur itself, [56,86,87] there are still huge unmet demands for the exploration in this aspect in terms of ubiquitous bacteria in normal life along with the efficiency, safety, and cost of such materials. Thus, a phosphorus-containing crosslinker - tristyryl phosphorus was developed (Figure S15) and the corresponding sulfur-rich polymers (poly(S-TSP)) obtained as usual via solvated IV with light, confirming by the characterization of FTIR, DSC, TGA, and PXRD (Figure S16). The antibacterial performance was subsequently conducted against *Gram-positive Staphylococcus aureus* and *Gram-negative Escherichia coli*, the most common infectious bacteria in hospitals, [88–90] by using the flat coating method and technology. [91–93] It was found that the antibacterial performance of poly(S-TSP) prevailed to *Gram-positive Staphylococcus aureus* at both low and high concentration of the materials, affording antibacterial rate of 64 % with 0.05 mg/mL concentration and 77 % with 0.2 mg/mL one (Figures S86–88). In contrast, only 20 % of antibacterial rate was achieved for *Gram-negative Escherichia coli* with the low concentration of materials under the same conditions.

2.4. Mechanistic aspects

A different reaction mechanism of free radicals with their excited states was proposed for the IV reaction with light irradiation supported by both the experimental and DFT simulation results. [73] The solution based Photoinitiated IV reaction presumably proceeds in the same manner. However, a sluggish reaction rate was observed for the photoinitiated IV reaction in solvents, contrasting to the common fast reaction rate for many photoinduced reactions. Therefore, the same reaction afforded yields of 18 %, 26 %, 31 %, 54 %, 75 %, and 80 % in 3, 5, 8, 12, 24, and 36 h reaction time, respectively (Table S6, Figure S89). Realizing the lack of fundamental understanding of the IV chemistry, we aimed to identify the origin of the toxic H_2S by-product first as there are no such by-products detected for photoinduced IV under both neat reaction conditions and in solvents. It is believed that the proton on the alpha-carbon of $\text{C}=\text{C}$ bonds in the crosslinkers dominates the generation of toxic H_2S by the sulfur radical and/or its ionic species attacking in the first step of the IV reaction. [10,13,14,37,93] The introduction of metal catalysts to the IV reaction inhibited the production of H_2S under thermal conditions, [37] whilst a complete elimination of it with light irradiation, [73] indicating alternative reaction pathways in operation for these reaction conditions. We pursued the use of saturated $\text{Pb}(\text{OAc})_2$ aqueous solution in an attempt to detect the production of toxic H_2S in this work. No H_2S by-product was detected for the current protocol with reaction between S_8 and BC in the solvents of toluene and CHCl_3 (Entries 1–8, Table 3, Figure S94). Of note is that the same reaction produced 141 mg PbS black precipitate under thermal condition at 130 °C in the presence of $\text{Zn}(\text{DTC})_2$ catalyst (2 wt%. Entry 9, Table 3, Figure S94a), demonstrating an alternative mechanistic pathway in operation between thermal and light irradiation. Surprisingly, there was only 9 mg of PbS black precipitate obtained for the same reaction in a dried solvent of toluene (Entry 10, Table 3, Figure S94b), implicating the presence of adventitious trace of water in solvents as the critical factor for the toxic H_2S production under thermal conditions.

Table 3

Summary of the results for the generation of toxic H_2S under different conditions^a.

Entry	Substrates ^b	Catal. ^c	Solvent ^d	Conditions and T / °C	H_2O / ml ^e	PbS / mg ^f
1	S_8 + BC	/	TL	r.t./365 nm	/	NO
2	S_8 + BC	/	TL (Dried)	r.t./365 nm	/	NO
3	S_8 + BC	/	CHCl_3	r.t./365 nm	/	NO
4	S_8 + BC	/	CHCl_3 (Dried)	r.t./365 nm	/	NO
5	S_8 (dried) + BC	/	CHCl_3	r.t./365 nm	/	NO
6	S_8 (dried) + BC	/	CHCl_3 (Dried)	r.t./365 nm	/	NO
7	S_8 (dried) + BC	/	TL	r.t./365 nm	/	NO
8	S_8 (dried) + BC	/	TL (Dried)	r.t./365 nm	/	NO
9	S_8 + BC	2 %	TL	130	/	141
10	S_8 + BC	2 %	TL (Dried)	130	/	9
11	S_8 (dried) + BC	2 %	TL	130	/	144
12	S_8 (dried) + BC	2 %	TL (Dried)	130	/	NO
13	S_8 (dried) + BC	2 %	TL (Dried)	130	0.1	NO
14	S_8 (dried) + BC	2 %	TL (Dried)	130	0.5	29
15	S_8 (dried) + BC	2 %	TL (Dried)	130	1.0	19
16	S_8 (dried) + BC	2 %	Xylene	130	/	10.2
17	S_8 (dried) + BC	2 %	Xylene (Dried)	130	/	6.3
18	S_8 (dried) + DIB	2 %	Xylene	135	/	13.5
19	S_8 (dried) + DIB	2 %	Xylene (Dried)	135	/	5.2
20	S_8 (dried) + MYE	2 %	Xylene	135	/	20.4
21	S_8 (dried) + MYE	2 %	Xylene (Dried)	135	/	17.2

^a). Reaction conditions: S_8 (1 g), β -carotene (BC, 1 g), solvent (20 mL) without catalyst at room temperature for 48 h under photoinduced polymerisation conditions and with $\text{Zn}(\text{DTC})_2$ (2 wt%) at 130 °C for 12 h under thermal conditions; S_8 (200 mg), DIB or MYE (200 mg) with $\text{Zn}(\text{DTC})_2$ (2 wt%) at 135 °C for 12 h under thermal conditions. The reaction flask was well-sealed and connected to the $\text{Pb}(\text{OAc})_2$ aqueous solution through a tube and needles to detect and collect the results of generation of toxic H_2S . DIB = 1,3-Diisopropenylbenzene, MYE = Myrcene.

^b). S_8 (dried) refer to S_8 was dried in a vacuum oven at 60 °C overnight prior to be directly used in the reaction.

^c). The catalyst used for the thermal conditions was $\text{Zn}(\text{DTC})_2$.

^d). The dried solvents were freshly distilled under reduced pressure after dried with CaH_2 for 24 h.

^e). Distilled water was used.

^f). The dark precipitate (PbS) was appeared once there was H_2S gas generated by the reaction and the resultant black precipitate was filtered, dried in an oven, and weigh out the amount obtained for each reaction, respectively.

We next attempted to systematically investigate the role of trace water in the reaction pathway. Primarily the results show there is no H_2S production for IV reaction with light irradiation under both dry and normal conditions (Entries 2,4,6,8 vs 1,3,5,7, Table 3); whilst there is no PbS black precipitate detected for the reaction with dried substrate and solvent under the same thermal conditions (Entry 12, Table 3). The addition of trace amount of distilled water into the absolute dry system could be used to probe the water issue in this protocol (Entries 13–15, Table 3). However, the obtained results are rather complicated even with a higher boiling point solvent of xylene to eliminate the possible vapour-leak issue of toluene at the reaction temperature, so were other

crosslinkers (Entries 16–21, Table 3). The more detailed investigation of role of water in IV is ongoing in our lab and will be published elsewhere in due course.

3. Conclusion

In summary, a simple and mild IV polymerisation with light irradiation in solvents at room temperature was developed for the first time, affording a broadened crosslinkers/monomers scope of alkenes and alkynes from gaseous to low boiling points, to high boiling points, and all the way up to solid state ones along with a unique resultant family of sulfur-rich polymers. The previous report on photoinduced IV, used only neat sulfur powder and liquid comonomer. [73] The absence of solvent in that system was shown to leave it susceptible to inhomogeneity in the products – as depending on the reactor geometry different areas would be subject to higher/lower irradiation. Solution synthesis might therefore allow a more viable route to production. The reactions underwent smoothly in solvents screened in this work and the resultant sulfur-rich polymers were fully characterized as equivalent to the analogues reported previously, affording good metal ion capture capability. The extension of crosslinkers to the value-added C5 fraction of industrial by-products demonstrated the significant advantage of the IV reaction in a solvated system, as similarly demonstrated with β -carotene. Reaction of sulfur with C5, without requiring purification to its components, would significantly lower cost industrially. β -carotene is solid at room temperature, so would have been challenging to react with solid sulfur by the photoinduced IV process in absence of solvent. A designed crosslinker exemplified the protocol and the resultant polymers showed good antibacterial performance with its coating derivative. The primary results of the mechanism investigation revealed the crucial role of unpremeditated trace water for the generation of toxic H₂S by-product under thermal conditions with more detailed work to be done in near future. Although light irradiation had previously been demonstrated as a method to form IV polymers, [73] the results reported here are the first to show it is possible to do this in solution and increase the breadth of the polymer systems shown. The increased diffusion in solution, and potential for agitation to be included in the future, provide greater homogeneity in the products, as well as allowing the room temperature reaction of co-monomers that would ordinarily by solid at such a temperature. The protocol developed in this research facilitates both the fundamental development of IV polymerisation and their potential applications with the unique functionalities of resultant polymers.

CRedit authorship contribution statement

Jinhong Jia: Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. **Peiyao Yan:** Investigation, Methodology, Validation, Writing – original draft. **Shan-shan Diana Cai:** Methodology, Validation, Formal analysis. **Yunfei Cui:** Formal analysis, Validation. **Xingwei Xun:** Formal analysis, Software, Validation. **Jingjiang Liu:** Validation. **Haoran Wang:** Formal analysis, Validation. **Liam Dodd:** Formal analysis, Validation. **Xiaolin Hu:** Validation, Software. **Daniel Lester:** Formal analysis. **Xi-Cun Wang:** Project administration. **Xiaofeng Wu:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing. **Tom Hasell:** Conceptualization, Supervision, Writing – original draft, Writing – review & editing. **Zheng-Jun Quan:** Conceptualization, Supervision, Funding acquisition, Resources, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors acknowledge the financial support from National Nature Science Foundation of China (NSFC, No. 22061038, 22067018), the Natural Science Foundation of Gansu Province (20YF3GA023), P.Y.Y., D.C., and H.R.W. thank the China Scholarship Council (CSC) for awarding their PhD Scholarships. T.H. supported by a Royal Society University Research Fellowship. The authors are very grateful to the Materials Innovation Factory (MIF) team members for their support in operating instruments. The authors also would like to thank Mr. Zhang Songsong from Shiyanjia Lab (www.shiyanjia.com) for the DSC analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2024.112815>.

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