



# The Role of Dithiocarbamate Catalysts in the Diversification of Sulfur Speciation Towards Anionic Sulfur

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# Metrics & More

ABSTRACT: Recently, there has been growing interest in the

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Supporting Information

implementation of various "catalysts" to further diversify the substrate scope for inverse vulcanization reactions. While there have been several proposals on the mechanism of how these catalysts work, the speciation of sulfur in these mixtures has remained elusive. As a key component to understanding when and if these catalysts are appropriate, we sought to elucidate the role of dithiocarbamate species in inverse vulcanization reactions by attempting to characterize the speciation of sulfur. The reaction efficacy for various substrates containing different functional groups we



efficacy for various substrates containing different functional groups with sulfur, either with or without a metal dithiocarbamate, potassium diethyldithiocarbamate (K-DTC), suggests the formation of a rapidly fluctuating sulfur speciation and, most importantly, *the presence of anionic sulfur*. The work concludes with some suggestions on best practices for the utilization of dithiocarbamate catalysts based on our results.

C ince its seminal publication in Nature Chemistry in 2013, O the field of inverse vulcanization (InV) has grown expansively.<sup>1</sup> Through the InV process, hybrid organicinorganic polymers can be synthesized by thermal homologation of elemental sulfur and its subsequent reaction with an organic olefin-chemistry that is akin to thiol-ene click chemistry (Scheme 1A). This process has drawn significant attention largely because of its ability to make use of elemental sulfur—a significant waste product of petroleum refining. The organic portion of the material can additionally be composed of low-value or waste products including triglycerides,<sup>2</sup> biopolymers,<sup>3-8</sup> and industrial waste products.<sup>9,10</sup> These materials are therefore generally low-cost and widely accessible. Many of these materials are additionally thermally healable and recyclable, owing to the thermally labile sulfursulfur bonds. Through InV, a wide variety of functional materials can be obtained including those for environmental remediation,<sup>11</sup> recyclable structural materials,<sup>5-7,12</sup> IR-transparent lenses, and as electrode materials for lithium-sulfur batteries.<sup>13–15</sup>

The development of this field has allowed for the expansion of the substrate scope in order to access new waste streams for valorization and generate more diverse advanced materials. Many of these strides have been aimed toward lowering the reaction temperature below traditional temperatures (160-180°C) to access a wider variety of volatile or thermally sensitive substrates. Toward this end, the implementation of ternary systems (first reported by Zhang et al.) has allowed for the incorporation of more thermally sensitive substrates.<sup>16,17</sup> Through this process an activated prepolymer can first be formed at traditional temperatures by reacting a thermally stable organic substrate with sulfur (Scheme 1B).<sup>16,17</sup> The formation of polysulfides in the prepolymer allows for sulfur– sulfur homologation at significantly lower temperatures. Thus, a thermally sensitive cross-linker can be combined with the activated prepolymer to allow for reaction at much lower temperatures (~100 °C). Even more recently, room temperature InV has been realized through a photoinduced process allowing for the reaction of sulfur with thermally sensitive and even gaseous organic olefins.<sup>18</sup> This method, however, is limited by inconsistent light penetration throughout the reaction media, preventing the potential for scalability.

In further efforts to expand the substrate scope of InV, Hasell et al. have published on "catalytic" InV in which various inorganic and organic catalysts have been examined.<sup>19–21</sup> Most notable of the selected catalysts are metal dithiocarbamates which have been used as "accelerators" in the rubber industry for decades.<sup>22–26</sup> In these reports, these catalysts allowed for more efficient conversion of "stubborn" olefinic substrates (i.e., not amenable to traditional InV routes), decreased reaction times and  $H_2S$  production, and improved polymer yield and thermal properties. Although unable to pinpoint an exact mechanism for this process, the authors indicated it may go through a radical, anionic, or some combination of the two

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Scheme 1. Development of the Field of Inverse Vulcanization: (A) Traditional Inverse Vulcanization between Sulfur and an Organic Olefin at 160–180 °C, (B) Low-Temperature Inverse Vulcanization through the Preparation of an Activated Prepolymer at Traditional Inverse Vulcanization Temperatures Followed by Reaction with a Volatile Comonomer at 90 °C, and (C) the "RASP" Process in Which Sulfur Can Displace an Aryl Halide at High Temperatures under N<sub>2</sub> (to Limit Oxidative Decomposition)



230 °C

processes.<sup>20</sup> It was later hypothesized in 2022 that these metal ul dithiocarbamate catalysts work by accelerating the rate of th radical formation thereby promoting the reaction of sulfur with th organic cross-linkers.<sup>18</sup> Since the seminal publication by re Hassell et al.,<sup>19</sup> numerous studies have been published utilizing sy metal dithiocarbamates in their formulations with good sa

success.<sup>18,27–30</sup> While many impactful developments in expanding the substrate scope of InV have been made, to date, primarily olefinic substrates have been utilized in conjunction with sulfur, significantly hindering the utilization of other waste streams and bioderived organic monomers. In 2020, however, Karunarathna et al. developed a synthetic methodology in which a very high-temperature (~230–240 °C) process could be utilized to facilitate the reaction of sulfur with aryl halides through a process coined "RASP" (radical aryl sulfur polymerization)—an exciting advancement but with very limited substrate scope owing to the high necessary temperatures (Scheme 1C).<sup>31,32</sup>

Based on the exemplary catalytic activity of metaldithiocarbamates published by Hasell and the historic precedent of using them as accelerators in vulcanization, this scaffold was selected for exploration in the present study. This work typifies obvious benefits to the field by expanding the substrate scope for InV to other untapped functional groups, providing some insight into how dithiocarbamate species catalyze the reaction of organic monomers with sulfur, and providing some suggestions on their use. Previous work has focused largely on zinc diethyldithiocarbamate, yet similar results have been obtained with other metal salts (Na, Cu, Co, Fe) indicating likely similar mechanistic pathways and making the selection of metal-salt inconsequential to the present study. Ultimately, the potassium salt (potassium diethyldithiocarbamate, **K-DTC**) was selected for probing because of the ubiquitous nature of potassium, its high solubility (and therefore ease of removal if so desirable at a later stage), and the ability to synthesize the catalyst at scale with materials readily accessible in most laboratories. **K-DTC** was therefore synthesized according to literature procedures to obtain the salt quantitatively in a 100% atom-economical process<sup>33</sup> (Scheme S1, Figures S1–3).

Since the conceptualization of InV in 2013, the mechanistic attributes have proven to be hard to experimentally quantify. Thus, most of the mechanistic insights have been deduced by studying reaction products through a litany of chemical analyses. This fact is emphasized by a recent publication by Pyun and co-workers showing that the initially proposed mechanism for the reaction of sulfur with the widely studied monomer, 1,3-diisopropenylbenzene, was incorrect, overturning 10 years' worth of precedent.<sup>34</sup> A thorough understanding of the speciation of sulfur above its ring-opening temperature remains elusive due to the short lifetime of radical sulfur species and the dynamic fluctuation of both ring and chain forms present in the melt.<sup>35</sup> One hallmark of sulfur above its ring-opening temperature is a drastic increase in viscosity, first reported by Tobolsky in 1964, and consistent with a wide range of polymeric sulfur species with varying degrees of chain length.<sup>36</sup> An interesting early observation in working with the K-DTC catalyst is that when added to molten sulfur at typical InV temperatures the viscosity reduces instantaneouslyindicating a change of sulfur speciation and/or a more rapid conversion between forms. This feature is interesting from both a mechanistic and a practical standpoint as high reaction viscosities can lead to poor mixing resulting in poor microstructure uniformities and perpetuating autoacceleration reactions.37

In order to better understand the catalytic nature of K-DTC, various substrates were selected with drastically different



Figure 1. Structures of compounds analyzed for their efficacy in the reaction with elemental sulfur. Their expected reaction sites are highlighted in red.

reactivities toward radical and anionic processes. In total, 5 different substrates were screened with 4 different functional groups, most being synthesized to generate monomers with high thermal stability so that they could be probed through as large as possible of a temperature range (Schemes S2–5, Figures S4–18). The functional groups analyzed consisted of an alkyl halide, an aryl halide, two allyl species, and a fluorinated olefin with potential applications in the preparation of advanced materials. The structures can be seen in Figure 1.

The analyses were conducted by preparing three-gram samples consisting of 90 wt % sulfur and 10 wt % organic monomer. When indicated, 1 wt % of the total system mass of **K-DTC** was employed (Scheme 2). This high-sulfur ratio was

Scheme 2. In the Absence of Catalyst, The Predominant Reactive Form Is Radical Sulfur, and In the Present Example of 1,6-Dibromohexane, This Would Not Be Expected to Lead to a Productive Reaction (A); Incorporation of K-DTC Allows Anionic Sulfur Species to Form; and the Two Would Be Expected to React in an  $S_N 2$ Type Pathway Resulting in Sulfur Incorporation with the Organic Monomer (B)



selected for a few reasons. First, most of the organic monomers utilized were high melting point solids, leading to high viscosity melts. Higher ratios of sulfur therefore led to decreased melt viscosities and better material homogenization. Second, decreased organic incorporation decreased the incidence of vitrification, allowing for wider temperature ranges to be probed. Finally, high-sulfur content composite materials typically have a  $T_g$  around -40 °C allowing for the facile probing of successful reaction with sulfur by DSC.<sup>3,38,39</sup> Thus, reactions were carried out at this selected sulfur: organic ratio and deemed "successful" when a  $T_g$  was observed. Although it

is possible that covalent carbon–sulfur bonds can form without the appearance of  $aT_{g}$ , its presence dictates the stabilization of polymeric sulfur via the formation of covalent sulfur–carbon bonds. Additionally, as the reaction proceeds and materials become more homogenized, the increase in  $T_{g}$  can indicate the quality of material produced (Table 1, Figures S19–28). Although all materials exhibited poor solubility in deuterated solvents, NMR analysis showed that when **K-DTC** allowed for reaction, stark differences in material solubility were observed (Figures S29–35).

The alkyl halide analyzed, 1,6-dibromohexane, was only expected to form covalent bonds with sulfur if anionic sulfur was present in the reaction mixture, as the formation of a  $1^{\circ}$ radical by halogen abstraction would be unlikely (Scheme 2). Hydrogen abstraction, on the other hand, could be a potential reaction pathway in the presence of radical sulfur but was not expected to lead to covalent C-S bonds. Sulfur was indeed not amenable to reaction with 1,6-dibromohexane when no catalyst was employed. With K-DTC, glass transitions were observed when the reaction was conducted in the temperature range of 180-210 °C. Glass transitions were not observable above this point, likely due to decomposition of the organic monomer. Attempts to recover  $T_g$  by curing overnight at 150  $^{\circ}\mathrm{C}$  were not successful. Comparative analysis of a material prepared at 190 vs 210 °C seemed to confirm this hightemperature decomposition hypothesis, although analysis proved challenging due to the rubbery nature of the sample prepared at 190 °C. The average of six runs of this sample revealed that the char yield at 600 °C was more than 3.5 times higher for the sample heated to 220 °C indicating likely precharring of the organic monomer at higher reaction temperatures (Figure S36A). IR analysis also seems to suggest high-temperature decomposition, demonstrating the aggressiveness of the reaction conditions when K-DTC is employed (Figure S36B).

Material prepared by heating at 190 °C for 2 h appeared as a red rubbery solid. Structural characterization of the prepared composite at 190 °C was accomplished by FT-IR and <sup>1</sup>H NMR with reasonable success. Due to losses of IR radiation by scattering from crystalline sulfur in the prepared material, characterization by this method proved challenging. To

synthesis T (°C)	diallyl-BPA		allyl-naphthol		1,6-dibromo- hexane		Me-Hy-2Br		Np-PFCP	
	no cat.	cat.	no cat.	cat.	no cat.	cat.	no cat.	cat.	no cat.	cat.
150	no T <sub>g</sub>	no $T_{\rm g}$	-28	-35	a	a	a	a	no T <sub>g</sub>	-40
160	-29	-23	-23	-30	no T <sub>g</sub>	no T <sub>g</sub>	a	a	no T <sub>g</sub>	-40
170	-17	-21	-24	-28	no T <sub>g</sub>	no T <sub>g</sub>	a	a	no T <sub>g</sub>	-40
180	a	a	-26	-31	no T <sub>g</sub>	-45	no T <sub>g</sub>	no T <sub>g</sub>	no T <sub>g</sub>	-40
190	a	a	-27	-33	no T <sub>g</sub>	-43	no T <sub>g</sub>	-39	no T <sub>g</sub>	-40
200	a	a	-31	-34	no T <sub>g</sub>	-38	no T <sub>g</sub>	-40	no T <sub>g</sub>	-40
210	a	a	a	a	no T <sub>g</sub>	-35	no T <sub>g</sub>	-39	no T <sub>g</sub>	no T <sub>g</sub>
220	a	a	a	a	a	a	-40	-36	a	a
230	a	a	a	a	a	a	-38	-37	a	a
240	a	a	a	a	a	a	-35	-36	a	a

Table 1.  $T_g$  Values (°C) for Composites Prepared from Sulfur (90 wt %) and the Indicated Organic Cross-Linker and K-DTC Catalyst When Indicated

<sup>a</sup>Sample not measured at this temperature.

quantify the extent and give insight into the mechanism of reaction, the changes in ratios between the major signals in 1,6dibromohexane were calculated. Stretching for C-H bonds at 1215, 1245, 1429, and 2933 cm<sup>-1</sup> were compared to the signal at 559 cm<sup>-1</sup> attributable to C-Br stretching. In all cases, a decrease in the ratios was observed, indicating fewer intact C-Br bonds in the material compared to the initial ratios found in the organic monomer (Figure S37 and Table S1). The average change in the ratios of signals was  $2.0 \pm 0.5$ , a value consistent with materials produced by the RASP process.<sup>40</sup> In order to remove interference from unreacted 1,6-dibromohexane, the material prepared at 190 °C was cryocrushed and thoroughly washed with CS<sub>2</sub>. This residual cross-linked material was only slightly soluble in deuterated pyridine due to its highly crosslinked nature. Several new peaks appeared in <sup>1</sup>H NMR including those for thiols ( $\sim$ 1.6 ppm), and those for methylene protons (-S-CH<sub>2</sub>-, 2.6-3.5 ppm) indicating reaction at the terminal ends. No significant signals were observed for methine protons (-S-CH-, 4.3-4.9 ppm) which would indicate more complicated radical H-abstraction pathways (Figure S38).<sup>16,35</sup>

The aryl halide analyzed, **Me-Hy-2Br**, was expected to react with sulfur regardless of the sulfur speciation. As has been previously reported in the literature, **Me-Hy-2Br** was found to react with sulfur when uncatalyzed at quite high temperatures.<sup>31,41</sup> In the present study, this substrate was found to react with sulfur at 220 °C and higher. Interestingly, when the **K-DTC** catalyst was employed, the reaction could be conducted successfully at as low as 190 °C. This improvement in reaction temperature provides obvious benefits by

expanding the potential substrate scope to more thermally sensitive comonomers. Comparative IR-analysis of the materials prepared at high and low temperatures proved challenging due to the change in numerous signals. Two bands due to Me-Hy-2Br were assessed (468, 1373 cm<sup>-1</sup>) as well as one band from  $S_8$  (1416 cm<sup>-1</sup>), but none gave quite perfect alignment. Qualitatively, though, there is a drastic decrease in the stretches associated with C-Br indicating the successful displacement of bromine with sulfur. Additionally, the signal attributable to the aromatic ester linkage (O=C-OR) at 1292 cm<sup>-1</sup> also decreased, suggesting that monomer decomposition had taken place (Figure S39). Further analysis by <sup>1</sup>H NMR confirmed this hypothesis. Dissolution in DMSO- $d_6$  at room temperature of both catalyzed and uncatalyzed samples (at 210 and 230 °C, respectively) revealed peaks corresponding to aromatic protons. Interestingly, the monomer, Me-Hy-2Br, is only partially soluble in boiling DMSO indicating successful disruption of the crystal lattice and modification with sulfur. While both spectra are almost identical, the spectrum corresponding to the catalyzed sample reveals a small but notable signal at ~9.4 ppm corresponding to liberated phenolic groups from the breakdown of the ester linkages, confirming the decomposition of the monomer structure in the presence of K-DTC (Figure S40).

An electrophilic fluoroolefin, a naphthyl-derivatized perfluorocylopentene (Np-PFCP), was analyzed for its ability to react with sulfur with and without the K-DTC catalyst. While known to undergo reaction with various nucleophiles under moderate conditions, there have been no known reports of its reactivity with radical species.<sup>42</sup> Attempts by co-workers to polymerize **PFCP** by thiol—ene click chemistry have also been unsuccessful, indicating its significantly improved reactivity under two-electron conditions. When assessed for its reactivity with sulfur, **Np-PFCP** was found only to react when a catalyst was present. Under these conditions,  $T_{\rm g}$ s were observed in reactions conducted in the range 150–200 °C. Similarly to 1,6-dibromohexane at higher temperatures, the  $T_{\rm g}$  was found to disappear, indicating likely decomposition.

Two composites were prepared from Np-PFCP, sulfur, and K-DTC: one below its reaction temperature (140 °C) and one above its lowest reaction temperature (180 °C). The materials were prepared by heating them at their respective reaction temperatures for 2 h. The two materials were assessed by several methods to confirm their expected reactivity. TGA revealed starkly different material properties. While both composites exhibit an initial mass loss step at 90–120 °C attributable to the loss of unreacted Np-PFCP, the mass loss for the sample prepared at 140 °C was found to be nearly 2.5 times larger at 135 °C (13.2 and 5.4% for materials prepared at low temperature and high temperature, respectively) further indicating successful monomer incorporation (Figure S41).

Allyl groups are well-known in the literature to polymerize well with sulfur. Two high boiling point systems were prepared for analysis with sulfur, a diallylated bisphenol (diallyl-BPA) and a monoallylated naphthol (allyl-naphthol), the latter to address higher temperature regimes which could not be probed with diallyl-BPA due to its vitrification.

For diallyl-BPA, a  $T_g$  was not visible until 160 °C. While the catalyzed sample produced a higher  $T_g$  material at this temperature, increasing the temperature to 170 °C saw the opposite trend. It is hypothesized that while the incorporation of **K-DTC** allows for more reactive sulfur species to form at lower temperatures (resulting in lower-temperature polymerizations) the equilibrium becomes more dynamic (faster), potentially sacrificing a narrow distribution of sulfur ranks. While these differences are quite small, they do seem to suggest that utilizing **K-DTC** at high temperatures could be detrimental to the production of a material with high microstructure uniformity.

Because allyl-naphthol did not vitrify as rapidly as diallyl-BPA, a larger temperature range could be probed, and the subtle pattern observed in the diallyl-BPA system was emphasized. Plotting the  $T_{g}$ s vs the reaction temperature revealed that in the absence of catalyst, the reaction seems to reach its  $T_{g}$  maximum at a lower temperature (Figure 2).



**Figure 2.** Comparison of materials prepared without (blue trace) or with (red trace) **K-DTC** suggests that a lower polydispersity of sulfur ranks may be obtained in the absence of **K-DTC**.

Although independent researchers have determined a correlation between sulfur rank and  $T_{gr}$  this finding seems to be inconsistent across different systems. Recent work shows that the sulfur rank polydispersity may be the culprit for variations in  $T_g$  where a lower polydispersity tends to lead to a higher  $T_{gr}^{43}$  It is therefore hypothesized that under these more moderate conditions (i.e., no accessible anionic sulfur), the optimal equilibrium conditions can be established at a lower temperature. For both systems, deviations from the optimal reaction temperature showed a decrease in  $T_g$ . Across the measured temperature range, uncatalyzed conditions produced slightly higher  $T_g$  materials, suggesting that it is not always advantageous to incorporate dithiocarbamate catalysts into InV formulations.

For both allyl systems, the materials prepared with and without catalyst were too similar to note any significant differences spectrophotometrically in these high-sulfur regimes and provides further explanation as to why previous attempts to gain mechanistic insights by probing olefinic systems have proven challenging. Thermally, the differences are interesting and may be even more significant with a larger incorporation of the organic material. It should therefore be considered best practice to do control experiments without catalyst and in a reasonable temperature range in order to determine some of the more nuanced effects at play for a specific monomer system.

The advancement of the field of InV has been largely predicated on the expansion of the substrate scope. While the utilization of DTC catalysts has previously shown to address "stubborn" olefinic monomers (like conjugated systems and acrylates), this work shows that DTC catalysts may uniquely and drastically expand the substrate scope of InV reactions by invoking anionic sulfur. Reactions with alkyl halides, aryl halides, and a fluorinated olefin that are unreactive under standard InV conditions have been shown to occur in the presence of K-DTC. Their use, however, should be approached with some level of trepidation as the conditions are significantly more aggressive than uncatalyzed conditions-especially at higher temperatures and with labile substituents (like saturated organics and esters). We propose that dithiocarbamate catalysts should not be used if the reaction can be done in its absence like in the case of electronically "normal" olefins (no strong electron-withdrawing groups or conjugation) as its incorporation may hinder the quality of the resultant material by disrupting the dynamic equilibrium sulfur rank and reducing material  $T_g$  values. Specifically, we believe dithiocarbamate catalysts should be considered for systems: (1) that require two-electron pathways for reaction to occur ( $S_N 2$ ,  $S_N Ar$ , etc.), (2) with electronically deficient pi-systems (acrylates, halogenated olefins, conjugated systems), and (3) with monomers that have poor compatibility with sulfur for its phase transfer catalyst ability.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.3c00607.

Experimental procedures; NMR spectra; DSC thermograms; TGA mass loss curves; FT-IR spectra; and GC-MS chromatograms (PDF)

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Moira K. Lauer: Conceptualization, Data curation, Investigation, Formal analysis, Validation, Methodology, Writingoriginal draft. Nicholas P. Godman: Supervision, Funding acquisition. Scott T. Iacono: Supervision, Funding acquisition, Writing-review and editing. All authors have given approval to the final version of the manuscript.

## Notes

The authors declare no competing financial interest.

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# NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on December 19, 2023, with an error in the title. The word 'toward' was corrected to 'towards'. The corrected version was reposted on January 2, 2024.