JOURNAL of THE TURKISH CHEMICAL SOCIETY
SECTION: A
CHEMISTRY
TURKISH CHEMICAL SOCIETY

# Understanding the Behaviour of Sulphur-Centred Radicals During Polymer Self-Healing

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**Abstract:** The high-level composite *ab initio* G3(MP2)-RAD method has been used to study the self-healing mechanism of materials based on thiuram disulfides and their derivatives (S=C(Z)S–SC(Z)=S, for Z = $CH_3$, $NEt_2$, $N(Et)CH_2CH_2OH$, Ph, Bz), and the effects of these Z-substituents on their efficacy. The relative contributions of cross-over and reversible addition fragmentation chain transfer reactions were ascertained, and the likelihood of chain-breaking side reactions was assessed. To rationalize the results, the various stabilisation energies of the radicals and closed-shell species were also evaluated. The study revealed that the self-healing mechanism of thiuram disulfides follows predominantly the cross-over reaction because of the high energies of intermediate radicals in the chain transfer mechanism. Based on the study, the most effective self-healing materials are predicted to contain amines as Z-groups, while those containing benzyl and its derivatives are most likely to undergo side reactions.

**Keywords:** Self-Healing polymers; thiuram disulfides; Radical Stabilisation energy.

**Submitted:** June 30, 2016. **Revised:** November 12, 2016. **Accepted:** November 15, 2016.

**Cite this:** Değirmenci İ, Coote M. Understanding the Behaviour of Sulphur-Centred Radicals During Polymer Self-Healing. JOTCSA. 2016;3(3):707–20.

**DOI:** To be assigned.

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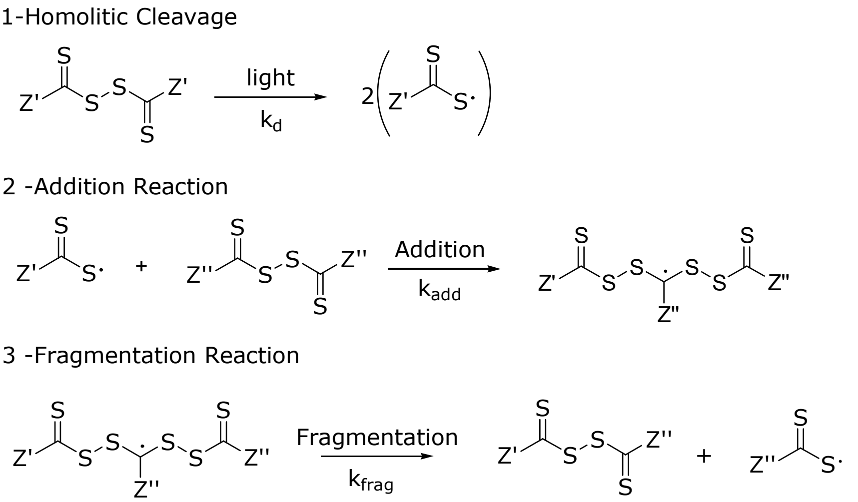
## INTRODUCTION

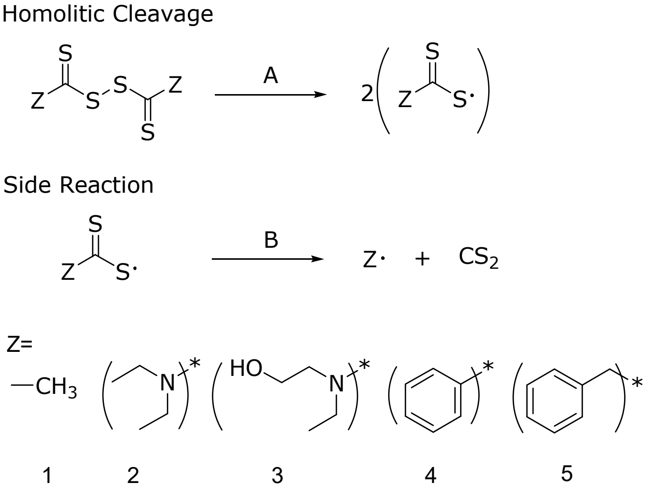
In recent decades, self-repairing or self-healing polymers have been developed so as to extend the working lifetime of materials [1-5]. They generally utilize non-covalent bonding networks [6, 7] or dynamic covalent bonds [8, 9] — special crosslinks that can be physically or chemically rearranged in response to external stimuli. Non-covalent bond forming systems are promising as self-repairing structures but tend to produce materials with weak mechanical strength [6, 7], whereas dynamic covalent systems tend to offer more mechanically stable polymeric materials [10]. Dynamic covalent systems utilise functional groups that are capable of reacting reversibly to form cross-links. They are designed so that the equilibrium position of the cross-linking reaction can be externally manipulated by chemical stimulation [11, 12], thermal stimulation [13-15] and photostimulation [16-18]. Photostimulation is especially promising for commercial applications as repair can occur at room temperature, is easy to handle, and targeted areas can be healed by limited exposure.

Recently, Amamoto *et al.* [16] introduced a covalently cross-linked polymer capable of undergoing visible light initiated self-healing. The photolabile groups in this system are thiuram disulfide linkages [19], which undergo S-S bond cleavage in the presence of light to produce sulphur-centred radicals that can either recombine or undergo a series of addition-fragmentation chain transfer reactions, reminiscent of the RAFT process (Scheme 1). In the latter case, the sulphur centred radical adds to the sulphur side of the S=C bond in another dithiuram linkage forming an intermediate radical that can then undergo β-scission, either to reproduce the reactants or a new "reshuffled" dithiuram linkage and a new sulphur-centred radical that can continue the process. The reshuffling of the covalent bond network can in principle occur purely by homolytic cleavage and subsequent recombination with a different sulphur-centred radical ("cross-over"), but is thought to contain significant contributions from the chain transfer processes. In particular, experimental studies in which light exposed samples are mixed with non-light exposed samples and then held in the dark demonstrate significant reshuffling over the course of several minutes, supporting not only a significant role for the radical transfer reaction but a relatively long half-life for the sulphur centred radicals [19] Earlier work by García-Con *et al.* [20] also supports a long lifetime (in excess of 2 weeks) for these types of radicals.



**Scheme 1.** Schematic representation of the reshuffling mechanism of DTS units.

Whilst these studies provide evidence for the role of chain transfer in the self-healing process, its relative extent (compared with cross-over) and its role improving the reshuffling efficiency is yet to be quantified. Understanding the mechanism of the self-healing process would be particularly useful in guiding the design of more efficient systems. Of particular interest is what role the thiocarbonyl substituent (Z in S=C(Z)S-S-R) plays in promoting cleavage and efficient reshuffling. At the same time, it is important to consider whether certain Z-groups might introduce an unwanted side reaction in which the sulphur-centred radical undergoes β-scission to produce $CS_2$ and Z• (Scheme 2). To address these questions in the present work, we use high-level *ab initio* molecular orbital calculations to study the key steps in the self-healing process for a variety of Z-groups, and use these in conjunction with relevant experimental data from the literature develop an *ab initio* kinetic model of the self-healing process.



**Scheme 2.** Schematic representation of homolytic bond cleavage and side reactions for the special substituent.

## COMPUTATIONAL METHODOLOGY

All geometry optimisations and single point energy calculations were carried out by using Gaussian 09 [21] and Molpro2009.1 [22] program packages. The recently developed DFT method (U)M06-2X/6-31G(d) level of theory [23] was chosen for the geometry optimisations and frequency calculations. Complete conformational searches were undertaken to ensure that the species were global rather than merely local minima. (U)HF and (U)MP2 methodologies at 6-31G(d) level were also tested during the transition state search for addition and fragmentation reactions. Improved energies were calculated using the high-level composite *ab initio* method G3(MP2)RAD [24] that approximates (UR)CCSD(T) calculations with a large triple-ζ basis from calculations with a double-ζ basis set, via basis-set corrections carried out at the R(O)MP2 level. A double-layer-ONIOM [25] approximation to G3(MP2)RAD in which remote substituent effects were evaluated with RMP2/GTMP2Large was used for the larger species. The accuracy of this level of theory for these types of species has been benchmarked previously [26, 27].

The electronic energies (E), geometries and vibrational frequencies ($v_i$) were then used to calculate the entropies (S), enthalpies (H) and Gibbs (G) free energies using the standard textbook formulae for the statistical thermodynamics of an ideal gas under the harmonic oscillator / rigid rotor approximation [28, 29] as follows.

$$G = H - TS \tag{1}$$

$$H = E + 4RT + \frac{R}{2}\sum_i \frac{hv_i}{k_B} + R\sum_i \frac{hv_i/k_B}{\exp(hv_i/k_BT)-1} \tag{2}$$

$$S = R\left(\ln\left(\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\frac{k_BT}{P}\right)+\frac{5}{2}\right) + R\left(\ln\left(\frac{\pi^{1/2}}{\sigma_r}\frac{T^{3/2}}{\left(\theta_{r,x}\theta_{r,y}\theta_{r,z}\right)^{1/2}}\right)+\frac{3}{2}\right) + R\sum_i\left(\frac{hv_i/k_BT}{\exp(hv_i/k_BT)-1} - \ln\left(1 - \exp\left(-\frac{hv_i}{k_BT}\right)\right)\right) + Rln(\omega_0) \tag{3}$$

where: $k_B$ is the Boltzmann constant, *h* is Planck's constant, *T* is the temperature, P is the pressure, M is the molecular weight, $\sigma_r$ is the rotational symmetry number, and $\theta_{r,i}$ are calculated from the *i* = x, y and z components of the principal moments of inertia $I_i$ of the optimized geometries as follows:

$$\theta_{r,i} = \frac{h^2}{8\pi^2 I_i k_B} \tag{4}$$

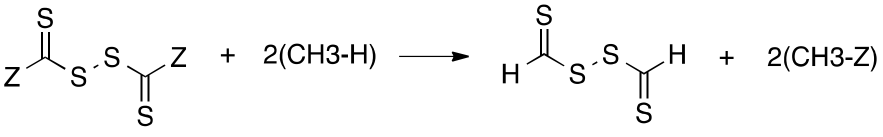
## RESULTS AND DISCUSSION

The first stage of the self-healing process is homolytic S–S cleavage of the thiuram disulphides (ZC(=S)S–S(S=)CZ), producing sulphur-centred radicals which can either trigger reshuffling or undergo an unwanted β-scission side reaction (see Scheme 2). The energetics of cleavage and β-scission as a function of the Z-group is summarised in Table 1. From these it can be seen that for the species studied, the side reaction is a relatively minor process, except where the Z-group is a benzyl moiety. In that case, the side reaction produces the highly stabilized benzyl radical [30, 31] and $CS_2$ and would prevent further self-healing from occurring. The other substituents resist this side reaction and are thus better suited to this application.

**Table 1.** Homolytic cleavage and side reaction energies at 298.15 K in kJ/mol at the G3(MP2)-RAD//M062X/6-31G(d) level of theory.

| | Homolytic cleavage | | Side reaction | | | |
|---|---|---|---|---|---|---|
| **Z** | **$\Delta H_{rxn}$** | **$\Delta G_{rxn}$** | **$\Delta H^{\ddagger}$** | **$\Delta G^{\ddagger}$** | **$\Delta H_{rxn}$** | **$\Delta G_{rxn}$** |
| $CH_3$ | 189.2 | 130.4 | 128.9 | 125.7 | 76.7 | 35.7 |
| $(C_2H_5)_2N$ | 155.0 | 98.3 | 166.1 | 158.7 | 118.9 | 66.6 |
| $(HOC_2H_4)N(C_2H_5)$ | 169.9 | 99.6 | 169.1 | 164.5 | 110.4 | 58.0 |
| Ph | 181.1 | 123.5 | 173.8 | 169.7 | 151.4 | 109.8 |
| Bz | 209.7 | 141.1 | 88.8 | 87.2 | 32.7 | -5.6 |

For the homolytic cleavage reaction, the nitrogen substituted reagents have the lowest bond dissociation energies (BDEs), followed by the methyl and then the benzyl. Lower enthalpies of the homolytic cleavage reaction for thiuram disulphides can be attributed to higher stability of the molecule structure and/or lower stability of the produced radical structure. The inherent stability of the thiuram disulphide agent can be qualitatively assessed from its agent stability energy (ASE) which is defined as the energy of the following isodesmic reaction:



(5)

The inherent stability of the radical can be assessed from its radical stabilization energy (RSE). In this work, two methods for assessing the RSE have been considered: the standard radical stabilisation energy ($RSE_{R\text{-}H}$, eq 6) and Zavitsas's inherent RSE method ($RSE_Z$, eq 7, [32]), which was introduced as a more universal definition of radical stability:

$$RSE_{R\text{-}H}\ (R\bullet) = D[H{-}CH_3] - D[H{-}R] \qquad (6)$$

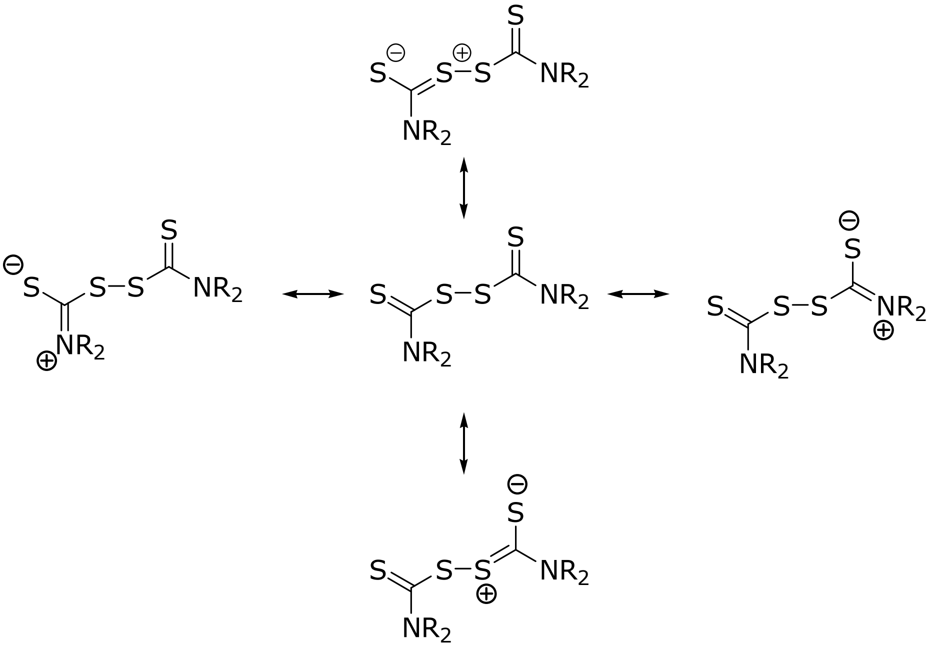
$$RSE_Z\ (R\bullet) = \tfrac{1}{2}(D[H_3C{-}CH_3]_{calc} - D[R{-}R]_{calc}) \qquad (7)$$

In order to calculate $RSE_Z$, the "strain free" R–R bond dissociation energies are calculated using Pauling's electronegativity equation [33] (see Refs [30, 31] for more details). Recently, this definition has been used successfully in various studies [30, 31, 34, 35] and has been recommended as being highly promising for comparing different classes radical on the same scale.

**Table 2.** Agent stability energies (ASE) and radical stabilization energies (RSE) energy values (kJ/mol) are calculated using G3(MP2)-RAD//M06-2X/6-31G(d) $\Delta H_{gas}$ values at 298.15 K

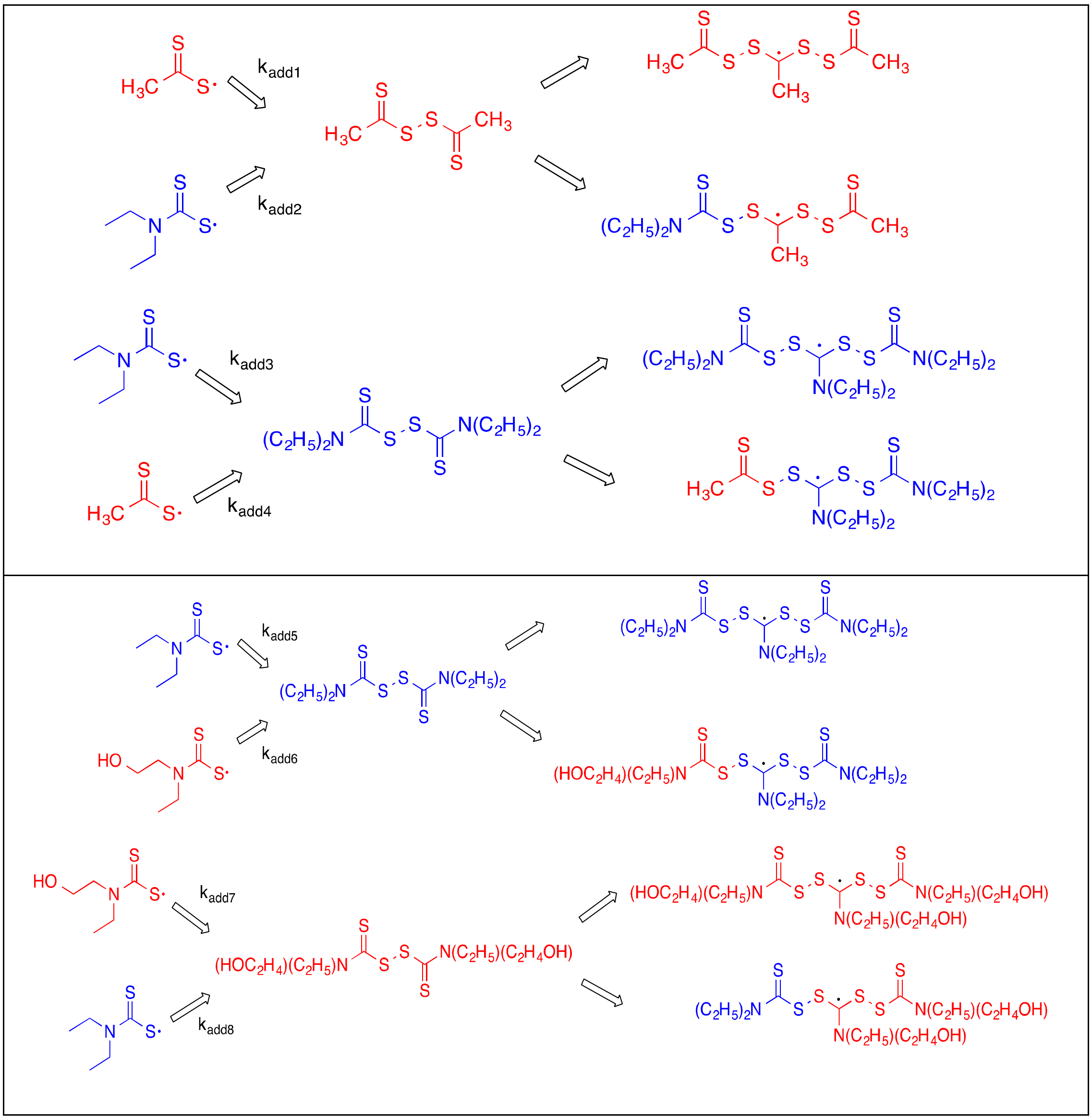
| **Z** | **ASE** | **$RSE_{R\text{-}H}$** | **$RSE_Z$** |
|---|---|---|---|
| $CH_3$ | 73.2 | 113.3 | 96.4 |
| $(C_2H_5)_2N$ | 180.4 | 128.9 | 116.0 |
| $(HOC_2H_4)N(C_2H_5)$ | 207.2 | 128.9 | 129.7 |
| Ph | 83.8 | 118.3 | 101.1 |
| Bz | 92.8 | 115.4 | 95.7 |

Values of the ASE, $RSE_{R\text{-}H}$ and $RSE_Z$ are provided in Table 2, from which it is seen that the nitrogen atom highly stabilizes both the agent and resulting radical, in both cases through resonance effects with the lone-pair donor nitrogen atom. Quantitatively, the stabilization of the agent is much larger than that of the radical, which would seem to indicate that the homolytic BDE should be larger for these compounds rather than smaller. Indeed, in a normal RAFT process [36], stabilization of the agent outweighs stabilisation of the radical and deactivates these reagents towards radical addition. However, here the homolytic BDEs for the nitrogen substituted agents are low implying the opposite is actually true. The low BDEs in this case are probably due to cross conjugation, which preferentially diminishes the stabilizing effect of the lone pair nitrogens on the disulfide agents (Scheme 3), and weakens these compounds compared to the other substituents. These interactions between substituents are not properly captured in the simplified ASE values.



**Scheme 3.** Cross conjugation in nitrogen substituted agents.

The second part of the reshuffling mechanism investigation is the addition of the produced radicals to the C=S double bond of the disulphide agents dithioacetate ($CH_3C(=S)S$-$SC(=S)CH_3$) (DTA) and tetraethylthiuram disulphide ($(CH_3CH_2)_2NC(=S)S$-$SC(=S)N(CH_2CH_3)_2$) (TETD). In the first case, the reshuffling of dithioacetate (DTA) and tetraethylthiuram disulphide (TETD) were taken into account. In the second case, the reshuffling of tetraethylthiuram disulphide (TETD) and diethyl dihydroxyethyl thiuram disulphide (DEDHETD) was modelled. The reactions studied are listed in Scheme 4. Add1, Add3 (= Add5) and Add7 can be classified as self-addition reactions and Add2, Add4, Add6 and Add8 can be classified as cross addition reactions. Conformational analysis for all reactants and dormant species were performed at the M06-2X/6-31G(d) level of theory. Unfortunately, establishing the addition transition state geometries at this level of theory was problematic due to the low or non-existent reaction barriers, as established previously [35] and below. Therefore, only reaction enthalpies and the Gibbs Free energies were calculated based on M06-2X/6-31G(d) geometries (Table 3). The G3(MP2)-RAD composite method was used to improve the energetics with ONIOM procedure. Interestingly, the addition reaction is much *less* exothermic than that of the carbon-centred radical addition to C=C double bond [37]. Indeed, addition reactions 6, 7 and 8 are actually endothermic. This contrasts with our recent study of simpler prototypical examples of these reactions, where thiyl radical addition to thioketones is strongly exothermic (by more than -50 kJ/mol) [35]. The conjugation with the sulphur substituents in the disulfides clearly deactivates the addition process in this case.



**Scheme 4.** Representation of the addition reactions and produced intermediates.

**Table 3.** Energetics (kJ/mol) and kinetics for the addition reactions in Scheme 4 at the G3(MP2)-RAD//M062X/6-31G(d) level.

| **Rxn #** | **Add1** | **Add2** | **Add3 (=Add5)** | **Add4** | **Add5 (=Add3)** | **Add6** | **Add7** | **Add8** |
|---|---|---|---|---|---|---|---|---|
| **$\Delta H_{rxn}$** | -40.15<br>(-39.82) | -27.05<br>(-26.19) | -23.80 | -29.24 | -23.80 | -7.43 | 3.31 | -6.59 |
| **$\Delta G_{rxn}$** | 8.24<br>(8.56) | 15.81<br>(16.68) | 18.44 | 12.96 | 18.44 | 40.70 | 53.65 | 38.20 |

An ONIOM approximation to G3(MP2)-RAD in which the core is studied at G3(MP2)-RAD and outer shell is calculated MP2/G3MP2Large was used. G3(MP2)-RAD calculations for full geometries are mentioned in brackets.

Due to the difficulty of locating the transition states using M06-2X/6-31G(d), *ab initio* methods were tested for further analysis. These methods tend to overestimate reaction barriers, whereas DFT methods tend to underestimate them, and hence it was thought that the *ab initio* methods should be better able to locate transition structures if they existed. The MP2/6-31G(d) method was used to locate the transition state geometries for the Add1 and the Add2 reactions. However, MP2 was not feasible for the other addition reactions due to the large size of the species involved. Therefore, the HF/6-31G(d) level of theory was chosen for consistently modelling all addition-fragmentation reactions (Table 4 and Figure 1). This level of theory is likely to overestimate reaction barriers and yet even here, the enthalpic barriers are either extremely low or submerged in the case of thiuram disulphide (TETD) with dithioacetate (DTA), indicating that pre-complexes probably play a role. Such submerged barriers have been noted previously for thiyl radical addition to C=S double bonds [35, 38-41] and arises because the high energy SOMO of the sulphur-centred radical is capable of the strong resonance interactions with the π* orbital of the substrate [35]. Overall there is a wide range of enthalpies depending on the Z-group, ranging from mildly exothermic to strongly endothermic, but importantly the Gibbs free energies of addition in all cases are positive, implying that addition is thermodynamically disfavoured and thus likely to be slow. When it does occur, fragmentation in either direction is expected to be fast and exergonic. Of the species studied, the lone pair donor substituted groups are again the most reactive to radical addition for the same cross-conjugation reasons outlined above.

**Table 4.** Energetics (kJ/mol) for the addition and fragmentation reactions in Scheme 4 at the G3(MP2)-RAD//HF/6-31G(d) level.

| | | **Addition** | | | | | **Fragmentation** | | |
|---|---|---|---|---|---|---|---|---|---|
| **Rxn #** | **d (Å)** | **$\Delta H_{rxn}$** | **$\Delta G_{rxn}$** | **$\Delta H^{\ddagger}$** | **$\Delta G^{\ddagger}$** | **$\Delta G^{\ddagger}$** | **$\Delta H_{rxn}$** | **$\Delta G_{rxn}$** | **$\Delta G^{\ddagger}$** |
| Add1 | 2.373<br>*2.444* | -18.40<br>(-18.90)<br>*-27.76* | 30.00<br>(29.51)<br>*24.39* | 3.83<br>(4.38)<br>*-9.89* | 48.01<br>(48.57)<br>*39.72* | 18.01 | 18.40 | -30.00 | 18.01 |
| Add2 | 2.390<br>*2.468* | -8.73<br>(-8.63)<br>*-15.58* | 34.39<br>(34.48)<br>*32.89* | 5.77<br>(9.40)<br>*-2.45* | 47.18<br>(50.81)<br>*44.31* | 19.26 | 5.66 | -35.83 | 19.26 |
| Add3 | 2.294 | 21.59 | 63.97 | -2.10 | 42.94 | -21.03 | -21.59 | -63.97 | -21.03 |
| Add4 | 2.387 | 19.22 | 63.37 | 8.58 | 54.53 | -23.34 | -36.28 | -72.44 | -23.34 |
| Add5 | 2.294 | 21.59 | 63.97 | -2.10 | 42.94 | -21.03 | -21.59 | -63.97 | -21.03 |
| Add6 | 2.293 | -6.13 | 39.34 | -38.76 | 12.61 | -10.51 | -45.08 | -80.88 | -10.51 |
| Add7 | 2.368 | -27.88 | 19.73 | -33.17 | 12.96 | -6.77 | 27.88 | -19.73 | -6.77 |
| Add8 | 2.362 | 2.66 | 46.68 | -8.32 | 37.57 | -12.87 | 13.54 | -36.44 | -12.87 |

ONIOM (the core shell is studied at G3(MP2)-RAD and outer shell is calculated MP2/G3MP2Large). Where available, G3(MP2)-RAD//HF-6-31G(d) calculations for full geometries are mentioned and G3(MP2)-RAD//MP2/6-31G(d) data are provided in italics.

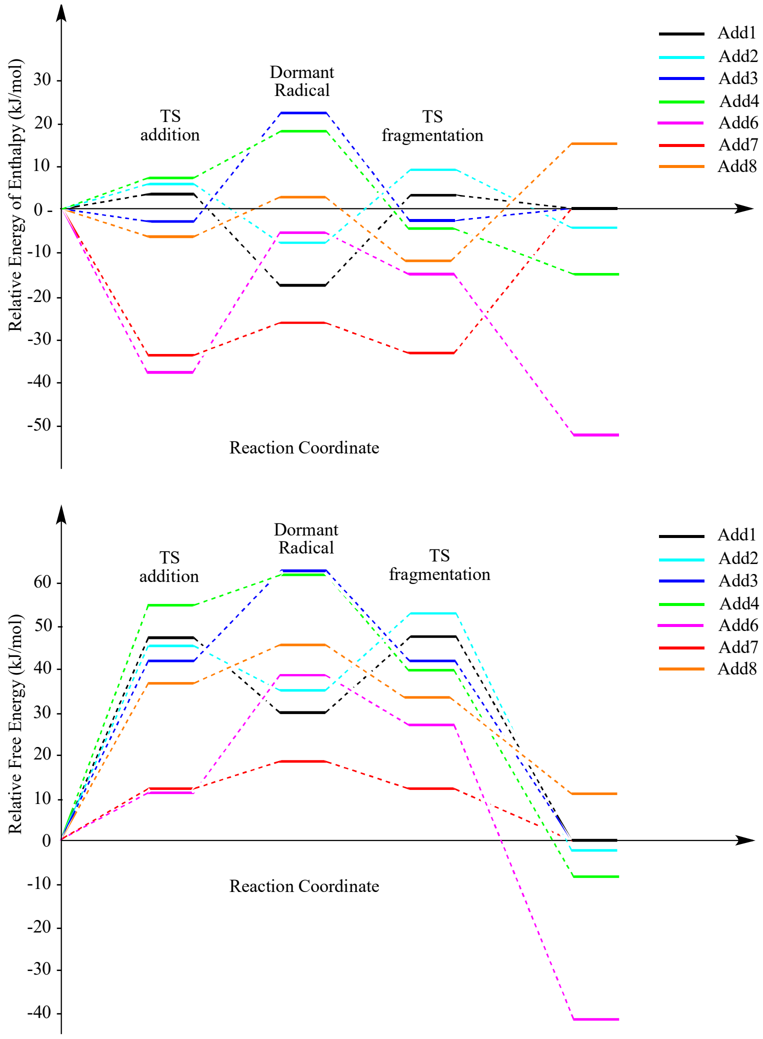


**Figure 1.** Relative enthalpies and free energies of reshuffling reactions at G3(MP2)-RAD//HF/6-31G(d) with ONIOM procedure.

## CONCLUSION

In this study, reshuffling mechanism of thiuram disulphides has been investigated using quantum chemical tools. Among the dithiodisulphides studied, dibenzyl dithioacetate was shown be subject to side reactions which render it unsuitable for these self-healing polymer applications. The remainder of the species are generally resistant to side reactions. The most reactive compounds, both to homolytic cleavage and addition-fragmentation reactions are the nitrogen substituted species. This arises from cross-conjugation effects, and suggests that these and other lone-pair donor substituted agents are the best candidates for self-healing materials. The re-shuffling mechanism itself can in principle proceed via both direct cross-over and addition-fragmentation. The calculations herein suggest that while addition fragmentation occurs with submerged reaction barriers, the process itself is relatively unfavourable due to the instability of the radical intermediate. Whilst full kinetic studies would be required to confirm this result, it is likely cross-over is the dominant pathway in the self-healing process.

## ACKNOWLEDGMENTS

I.D. gratefully acknowledges the Scientific and Technological Research Council of Turkey (TUBITAK) under 2219 grant. M.L.C gratefully acknowledges generous allocations of supercomputing time on the National Facility of the Australian National Computational Infrastructure and financial support from the Australian Research Council Centre of Excellence for Electromaterials Science. Many useful discussions with Professor Krzysztof Matyjaszewski are also gratefully acknowledged.

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### Türkçe Öz ve Anahtar Kelimeler

## Polimer İyileşmesi Sırasında Kükürtlü Radikallerin Davranışını Anlamak

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**Öz:** Yüksek seviye kompozit *ab initio* G3(MP2)-RAD yöntemi tiuram disülfürlerin ve türevlerinin (S=C(Z)S–SC(Z)=S, Z = $CH_3$, $NEt_2$, N(Et)$CH_2CH_2OH$, Ph, Bz) kendi kendine iyileşme mekanizmasını çalışmakta kullanılmıştır ve bu Z sübstitüentlerinin etkinlik üzerindeki etkileri çalışılmıştır. Cross-over ve tersinir katılma kısımlanma zincir iletim tepkimelerinin relatif olarak katkıları bulunmuş ve zincir kırılma yan tepkimelerinin olasılığı değerlendirilmiştir. Sonuçları rasyonelize etmek için, radikallerin ve kapalı kabuki türlerinin çeşitli kararlılaşma enerjileri değerlendirilmiştir. Çalışma, tiuram disülfidlerin kendi kendine iyileşme mekanizmasının baskın şekilde cross-over tepkimesi üzerinden gittiğini göstermektedir, çünkü zincir iletim mekanizmasında ara radikallerin enerjisi yüksektir. Çalışmaya dayanarak, en etkili kendi başına iyileşme sağlayan malzemelerin Z grubu olarak amin taşıdığı bulunmuştur; benzil ve türevlerini içeren yan grupların ise yan tepkimelere yol açtığı anlaşılmıştır.

**Anahtar kelimeler:** Kendi kendine iyileşen polimerler; tiuram disülfidler; radikal kararlılaşma enerjisi.

**Sunulma:** 30 Haziran 2016. **Düzeltme:** 12 Kasım 2016. **Kabul:** 15 Kasım 2016.