NMR and EPR Structural Analysis and Stability Study of Inverse Vulcanized Sulfur Copolymers

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This supplementary information is intended to provide additional details on the following issues reported in the manuscript:

1. Sample preparation and characterization.
2. $^1$H NMR spectra of the DIB monomer and of sulfur copolymers with different weight percentage of DIB.
3. $^1$H-$^{13}$C CP MAS spectra of model polymer polypropylene-isotactic (PPI)
4. $^1$H NMR in CDCl$_3$
5. $^{13}$C DEPT 135 spectra of S-DIB-30-70
6. FTIR spectra of monomer and S-DIB copolymer
7. DSC and XRD of pure elemental sulfur
8. DSC and XRD of S-DIB copolymers
1. SAMPLE PREPARATION

The reaction of sulfur with DIB at 180 °C results in the formation of highly cross-linked sulfur copolymers.

A schematic representation of the synthetic procedure is presented in Scheme S1.

![Scheme S1. Schematic diagram of S-DIB copolymer synthesis. The picture shows the products of the reaction using different S-DIB ratios: S-DIB-90-10, S-DIB-70-30, S-DIB-50-50, S-DIB-30-70, and S-DIB-10-90 respectively (left to right).](image)
2. $^1$H SOLID – STATE MAS NMR SPECTRA OF SULFUR COPOLYMERS.

Solid-state $^1$H NMR measurements were run on a Bruker AVANCE 400 ($B_0 = 9.4$ T) spectrometer operating at 400.23 MHz for $^1$H. Spectra were recorded at room temperature using cylindrical 4 mm o.d. Zirconia (ZrO2) rotors. $^1$H NMR experiments were carried out at the spinning speed of 12 kHz.

![Solid state $^1$H NMR spectrum of DIB monomer and S-DIB copolymers with different weight percentage of DIB.

$\textbf{Figure S1.}$ Solid-state $^1$H NMR spectrum of DIB monomer and S-DIB copolymers with different weight percentage of DIB.

Solid state $^1$H NMR spectra of the sulfur copolymer prepared by varying the weight ratio of DIB (30, 50 and 70 wt %) with respect to sulfur are shown in Figure S1. The spectral lines were very broad. Only two lines appeared, corresponding to aliphatic and aromatic protons.
3. $^1$H-$^{13}$C CP MAS SPECTRA OF MODEL POLYMER POLYPROPYLENE-ISOTACTIC (PPI)

**Figure S2.** $^1$H-$^{13}$C CP MAS spectra of model polymer polypropylene-isotactic (PPI) (a) with polarization inversion (PI=38µs) and without polarization inversion (PI=1µs), for long (CT=2ms) and short (CT=50µs) contact times respectively. (b) CP-TOSS spectra of the PPI for different values of the contact time (CT) ranging from 2000µs to 50 µs.

Cross-Polarization-Polarization Inversion (CPPI) technique is commonly applied for MAS spectral editing. In this method, it is possible to distinguish between $^{13}$CH and $^{13}$CH$_2$ as well as $^{13}$CH$_3$ and non-protonated carbon signals depending on the polarization inversion time. Polypropylene isotactic (PPI) polymer containing $^{13}$CH, $^{13}$CH$_2$ and CH was chosen as a model polymer to test the performance of the CPPI pulse sequence before applying the technique on the S-DIB copolymers. The experiment was carried at low MAS speed of 5 kHz with polarization inversion times PIT=38 µs and PIT=1 µs. Without polarization (PIT =1 µs) CPPI spectra of PP
showed all three major peaks at $\delta = 27.1$ ppm, $\delta = 31.5$ ppm and $\delta = 49.3$ ppm respectively, corresponding to $^{13}$C peaks of $^{13}$CH$_3$, $^{13}$CH, and $^{13}$CH$_2$ groups respectively. However, by increasing the polarization inversion time to PIT = 38 $\mu$s, the $^{13}$CH peak disappeared completely; the $^{13}$CH$_2$ peak was inverted whereas, the $^{13}$CH$_3$ peak was unaffected. Thus, a CPPI pulse sequence with similar parameters was applied to S-DIB samples in order to distinguish between carbon nuclei belonging to different groups.

4. $^1$H NMR in CDCl$_3$
Figure S3 $^1$H NMR spectra of sulfur copolymer with different weight ratio of sulfur compared with DIB monomer, the highlighted area shows the peak for thiol group.
Figure S4. $^{13}$C proton decoupled spectrum (top) and $^{13}$C DEPT 135 spectra (bottom) of S-DIB-30-70; the inset shows the enlarged area from 40 to 60 ppm. Positive signals are due to CH and CH$_3$ groups; negative signals are due to CH$_2$ groups; quaternary carbons are suppressed.
5. FTIR SPECTRA OF DIB MONOMER AND S-DIB COPOLYMERS

Figure S5. FTIR spectra of pure DIB (—) and S-DIB copolymers with 50 wt % (—) and 30wt % (—) of DIB.

According to the assignment of the absorption peaks observed in the C–S copolymer-20%DEB-2h composite, the peaks observed at 1128.5, 1015 and 700 cm$^{-1}$ can be assigned to C-S bonds (absent in DIB).
6. XRD and DSC Characterization of Elemental sulfur

Figure S6. a) DSC thermogram of elemental sulfur under nitrogen atmosphere taken in two cycles with a heating rate of 10 °C/min and b) the XRD pattern of elemental sulfur.

Pure elemental sulfur shows two transitions in the first heating cycle and one transition in the first cooling cycle. In the first heating cycle, elemental sulfur undergoes solid-solid transition from orthorhombic crystal to monoclinic crystal at 109 °C and with further heating, it undergoes melting at 119 °C and ring opening polymerization at 175 °C. When sulfur is cooled, it shows a
single sharp transition at 52 assigned to a crystallization of sulfur. However in second heating cycle sulfur shows only one melting transition around 120 °C, this could be due to the absence of orthorhombic phase after first cycle. The presence of melt and crystallization transition in the elemental sulfur suggests the crystalline nature of the sulfur. This was also further supported by the appearance of characteristic crystalline diffraction peaks of sulfur located at 23.1, 25.9, 27.8, and 28.68 in XRD.

7. XRD and DSC Characterization of S-DIB copolymer

The sulfur copolymer (S-DIB) prepared with the different compositions are subjected to DSC and XRD study.

8i. DSC study

Differential Scanning Calorimetry was carried out on Discovery Series DSC (TA instruments) under nitrogen atmosphere and in the temperature range between -30°C to 200°C. DSC measurements were taken in two cycles with a heating rate of 10°C/min. The corresponding thermograms of S-DIB samples with various weight percentages of DIB are presented in Figure S7.

The glass transition temperature (Tg) of the copolymers is observed to increase by increasing the DIB content. The samples containing more than 30 wt % of cross-linker did not show any melting transition this suggests that the crosslinking reaction between sulfur and DIB is complete and leads to the formation of stable amorphous copolymers. On the other hand, the samples with low amount of cross-linker showed a melt transition peak at ~119 oC, which is similar to the melt transition of pure elemental sulfur (see Figure S6). This suggests the presence of small
amount of crystalline sulfur in the copolymer. However, during the second heating cycle the melt transition is significantly suppressed, indicating that the elemental sulfur under goes polymerization and reforms copolymer with DIB under first heating cycle.

Figure S7. S-DIB-90-10 samples prepared under similar conditions a) digital image of freshly prepared samples showing bright orange color with uniform sulfur DIB distribution, b) digital image of the same sample after two months of aging at room temperature, showing the change of color from bright orange red to dull orange red and the appearance of partially recrystallized sulfur on the surface, c) DSC thermograms and d)XRD patterns respectively of aged S-DIB copolymers with various weight percentages of DIB.

The appearance of msulfur melt transition can be explained based on the amount of cross-linker. Evidently, lower amount of DIB results in a lower degree of crosslinking with the sulfur, which leading to the formation of long chains of sulfur. These long sulfur chains are unstable at
room temperature similar to the polysulfur and slowly undergo depolymerization and finally results in the partial formation of elemental sulfur. Whereas, the copolymers with higher amount of DIB results in high crosslinking density with shorted sulfur chain length. These short cross-linked sulfur chains form stable amorphous copolymer. Thus, the copolymer with higher amount of cross-linker did not show any melt transition corresponds to sulfur. From Figure S7 a and b, its clearly observed that the freshly prepared copolymer (Figure S7a) are bright orange in color, however over the time the intensity of the color decreased and yellow spots started to appear on the samples. The decrease in the color also indicate the partial depolymerization and the yellow spots are from depolymerized elemental sulfur from the copolymer.

8ii. XRD study

The XRD patterns of the synthesized S-DIB samples with various weight percentages of DIB are shown in figure S7d. The sample with the least amount of DIB (10 wt %) shows low intensity peaks corresponding to sulfur, the sulfur could be arising from the partial depolymerization of amorphous copolymer to elemental sulfur. Whereas the samples with high DIB content are completely amorphous, and did not show any sharp peaks suggesting the complete conversion of crystalline sulfur into amorphous copolymer. These XRD results are in good agreement with the DSC experiments and confirm the partial depolymerization of sulfur copolymer which results in the elemental sulfur.
REFERENCES

1. Sun, Z.; Xiao, M.; Wang, S.; Han, D.; Song, S.; Chen, G.; Meng, Y., Sulfur-Rich Polymeric Materials with Semi-Interpenetrating Network Structure as a Novel Lithium-Sulfur Cathode. *Journal of Materials Chemistry A* **2014**, *2*, 9280-9286.