Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Sulfur-Dipentene polysulfides: from industrial waste to sustainable, low-cost materials

Selena Silvano[a,b,c], Incoronata Tritto[b], Simona Losio[b], Laura Boggioni[b]

[a)] *University of Milano Bicocca, Dep. Materials Science, via R. Cozzi, 55, 20125 Milano (Italy)*

[b)] *CNR-SCITEC, Istituto di Scienze e Tecnologie Chimiche "Giulio Natta", via A. Corti, 12, 20133 Milano (Italy)*

[c)] *INSTM, Via Giuseppe Giusti, 9, 50121 Firenze (Italy)*

email: incoronata.tritto@scitec.cnr.it

Comparison of stability of poly(S-dipentene) and poly(S-dipentene-DAS)

Figure S1a and Figure S1b show the bottom of reaction flasks of entry 4 and entry 9 after 36 h; it is visible that poly(S-Dipentene) became inhomogeneous (sulfur bloom showed in Figure S1a) while poly(S-dipentene-DAS) did not show any depolymerization phenomena (Figure S1b).

The solubilization of aged (36 h) poly(S-Dipentene) in chloroform showed a sulfur deposit (Figure S1c) on vial bottom which indicates the depolymerisation of sulfur and its return to S8 crystals. The solubilized aged (36 h) poly(S-Dipentene-DAS) did not reveal any sulfur deposit (Figure S1d).

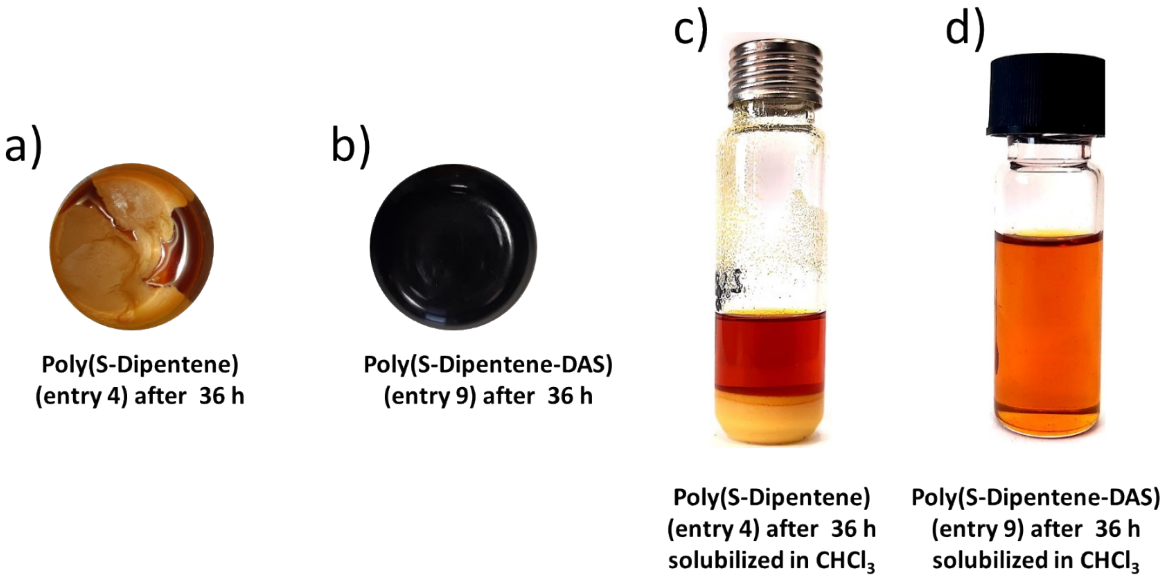

Figure S1: Comparison of the stability of poly(S-dipentene) and poly(S-dipentene-DAS) after 36 h: sample as is (Figures S1a and S1b) and sample after solubilization in chloroform (Figures S1c and S1d)

Preparation of a film of poly(S-Dipentene-DAS)

3 g of the poly(S-Dipentene-DAS) synthesized according to the general procedure, were transferred on 10 cm Petri dish and heated at 80 °C for 10 minutes and then cooled to room temperature. The film of the molten polysulfide on dish surface results transparent, as shown in Figure S2.

Figure S2: Film of poly(S-Dipentene-DAS)

Preparation of objects of poly(S-Dipentene-DAS)

The poly(S-Dipentene-DAS) was synthesized according to the general procedure. The polysulfide was melted by heating the material at 80°C, poured into a silicone mould and cooled to 4 °C. Figure S3 shows the object formed.

Figure S3 Moulded object made of poly(S-Dipentene-DAS).

Metal chloride (aq) removal using the blend PS-poly(S-Dipentene-DAS) 50 wt %

Water solutions containing 100 ppm of metal chloride were prepared for the following inorganic salts: $FeCl_3$, $CuCl_2$, $CrCl_2$, $NiCl_2$ and $CoCl_2$.

An aliquot of $FeCl_3$, $CuCl_2$, $CrCl_2$, $NiCl_2$ and $CoCl_2$ solution (about 20 mL) was placed on ground blend PS-poly(S-Dipentene-DAS) and incubated for 24 hours (Figure S4).

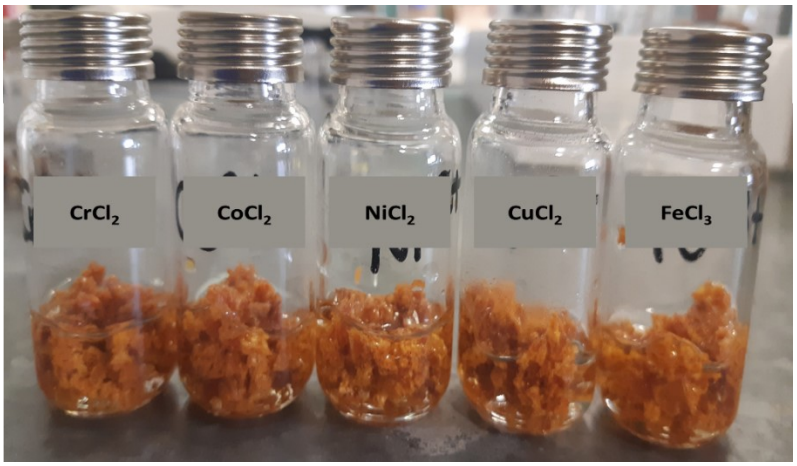

Figure S4

After 24 h, some drops of solution were placed on both poly(S-Dipentene-DAS) (entry 9) as prepared (Figure S5a) and after 24 h (Figure S5b). The samples were incubated at 4 °C to detect change in colour. No colour change appeared after 24 h.

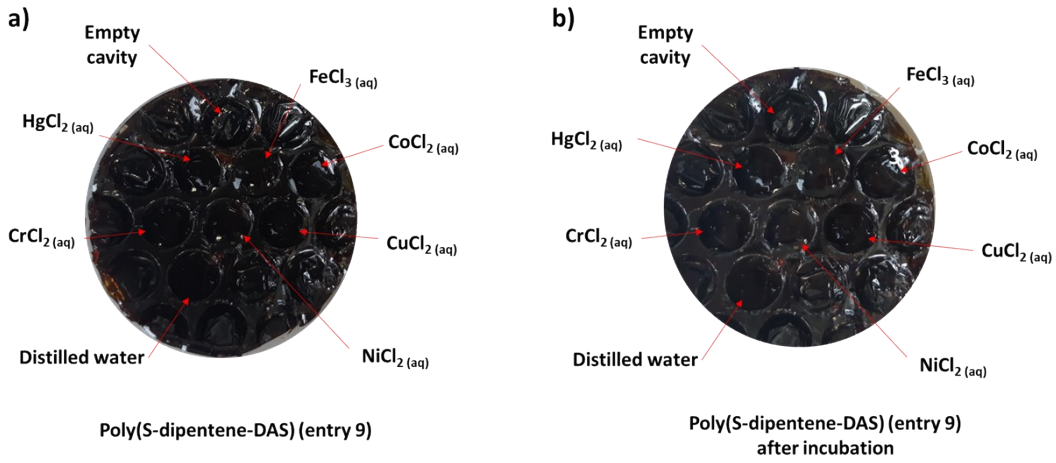

Figure S5

Elemental analysis of poly(S-Dipentene), poly(S-Dipentene-DAS), and blend PS-Poly(S-Dipentene-DAS)

The elemental analysis was carried out at University of Milan (Italy). Carbon, hydrogen, nitrogen content (wt %) was determined by using CHN Perkin Elmer 2400SERIESII. Sulfur content (wt %) was calculated by the equation below:

$$S wt\% = 100 - C\ wt\% - H\ wt\% - N wt\%$$

Results of elemental analysis of poly(S-Dipentene), poly(S-Dipentene-DAS), and blend PS-Poly(S-Dipentene-DAS) are reported in Table S1

Table S1 Elemental analysis results

Sample	C (wt %)	H (wt %)	N (wt %)	S (wt %)
Poly(S-Dipentene)	30.23	3.98	0.02	65.77
Poly(S-Dipentene-DAS)	32.22	4.13	0.03	63.62
Blend PS-Poly(S-Dipentene-DAS)	61.45	5.79	0.14	32.62

Gas chromatography-mass spectrometry (GC-MS) of volatile compounds of poly(S-Dipentene)

GC-MS was carried out on Agilent 7890A GC and 5975C VL MSD detector using Agilent HP-5ms UI column (30 m long × 25 mm film thickness × 0.25 mm ID). Method: isothermal heating at 37 °C for 10 min, heating to 250 °C at 10 °C/min and held at 250 °C for 10 min. Sample split equal to 30:1 and gas flow rate 34 mL/min. The head vapours (0.1µL) of poly(S-Dipentene) (entry 4) after 5 h of reaction and dipentene monomer have been injected.

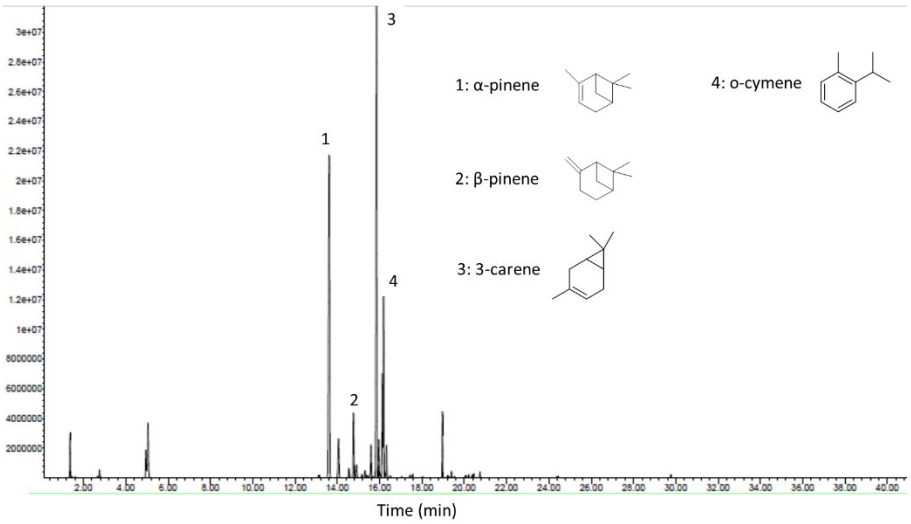

Figure S6 GC-MS of volatile compounds of poly(S-Dipentene) (entry 4)

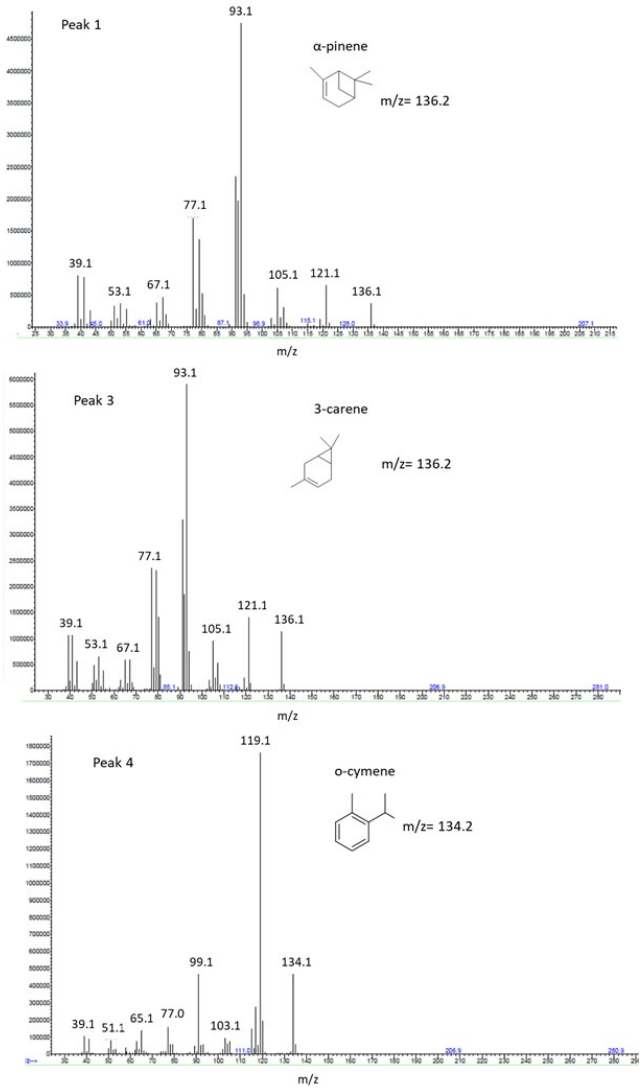

Figure S7 MS fragmentation of peaks 1, 3 and 4 of Figure S6 attributable to α-pinene, 3-carene and o-cymene, respectively.

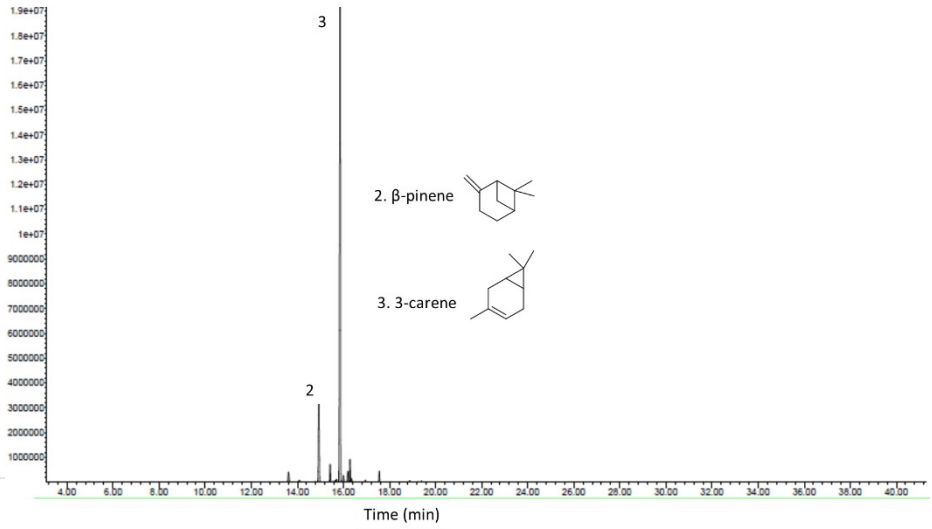

Figure S8 GC-MS of dipentene

The main components of head vapours were attributable to α-pinene (peak 1, Figure S6), 3-carene (peak 3, Figure S6) which were contained in dipentene and o-cymene (peak 4, Figure S6) as major by-product formed by inverse vulcanization reaction. The comparison between GC-MS analysis of head vapours (Figure S6) and dipentene (Figure S8) clearly shows that 3-carene component of dipentene is most reactive than α and β pinene.

SEM analysis of polystyrene-poly(S-Dipentene-DAS)

Scanning electron microscopy (SEM) images were recorded by SEM-EDX TM1000 Hitachi at University of Milan. The samples have been coated with gold nanoparticles before to record SEM images.

The salt templating of polystyrene-poly(S-Dipentene-DAS) blend with 50 wt % of polystyrene produced inhomogeneous and irregular macropores (Figure S9a). SEM showed sulfur microcrystals characterized by an angular shape (Figure S9b) which appear as little bright spherical dots homogeneously distributed on material surface (Figure S9c). Presence of small amount of unreacted sulfur has not influence on thermal properties. (Sulfur crystallization peak was not observed from DSC analysis.)

After usage of the hot press, a quite smooth surface, without phase separations and pores was formed (Figure S9d). Superficial elemental sulfur crystals seemed to disappear, probably by a post cross-linking reaction. Moreover, the polysulfide blend showed thin cracks when the hot press was used (Figure S9e).

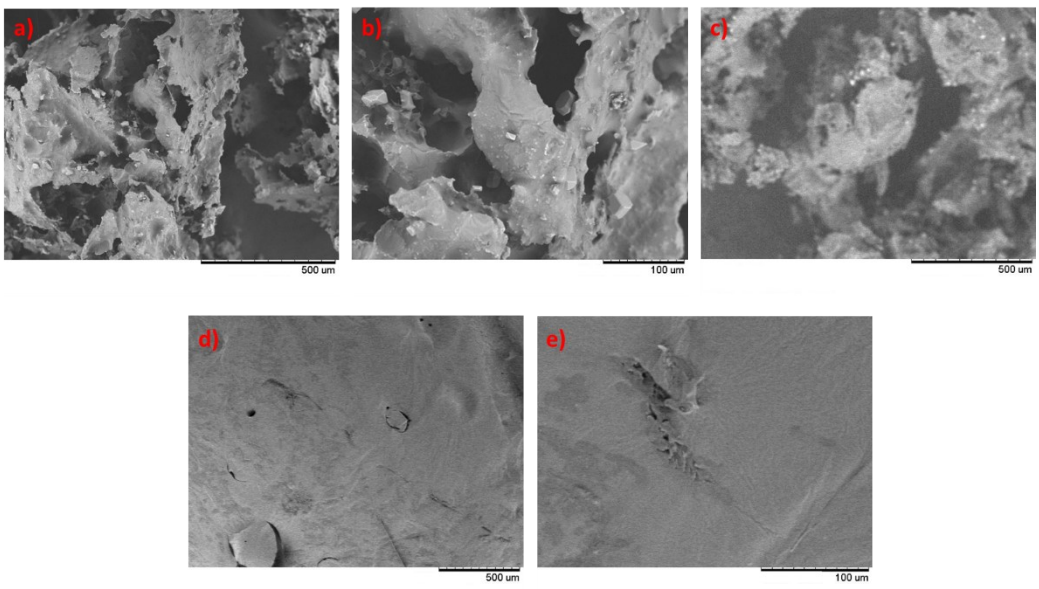

Figure S9: SEM images of polystyrene-poly(S-Dipentene-DAS) blend with 50 wt % of polystyrene: metalated after salt templating at magnification x200 (a) and at magnification x600 (b) and recorded without sample metalation at magnification x200 (c); after hot press at magnification x200 (d) and at magnification x600 (e).