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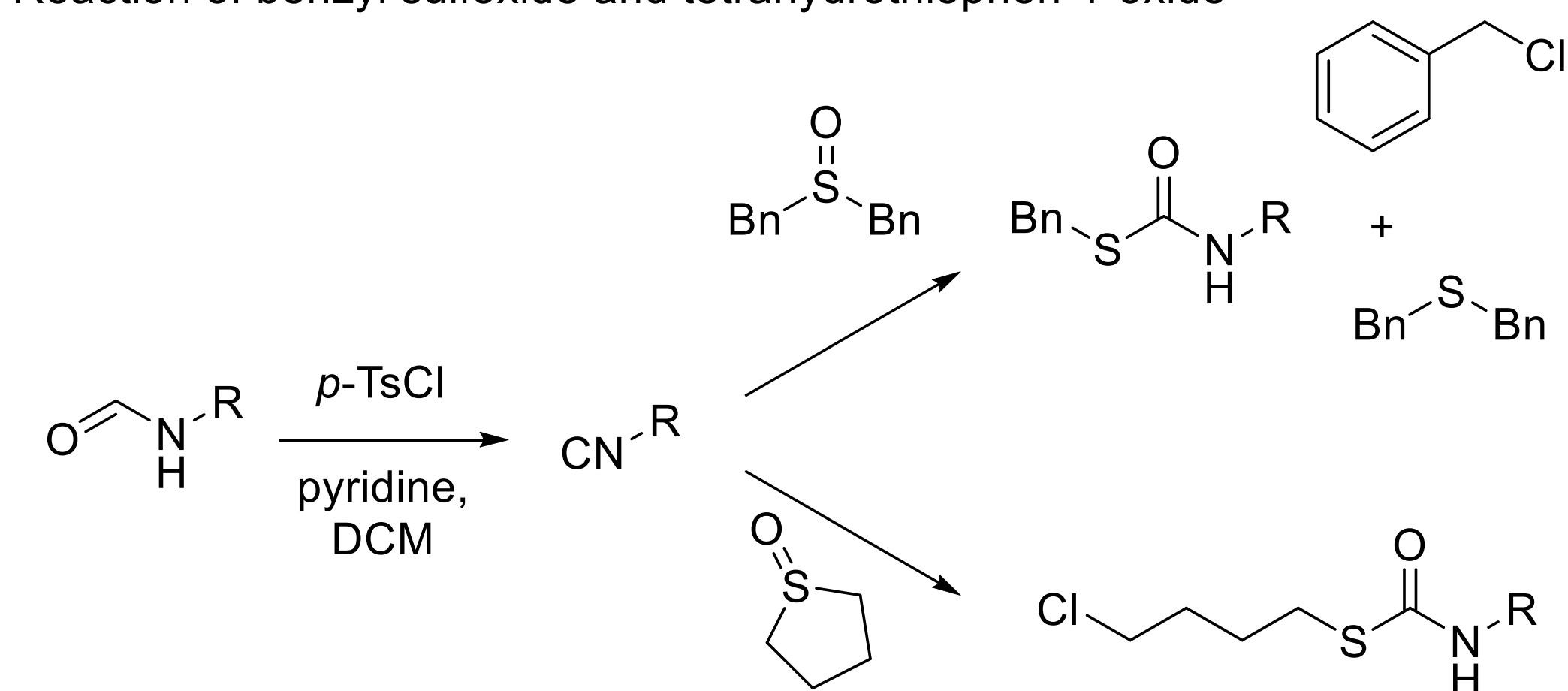
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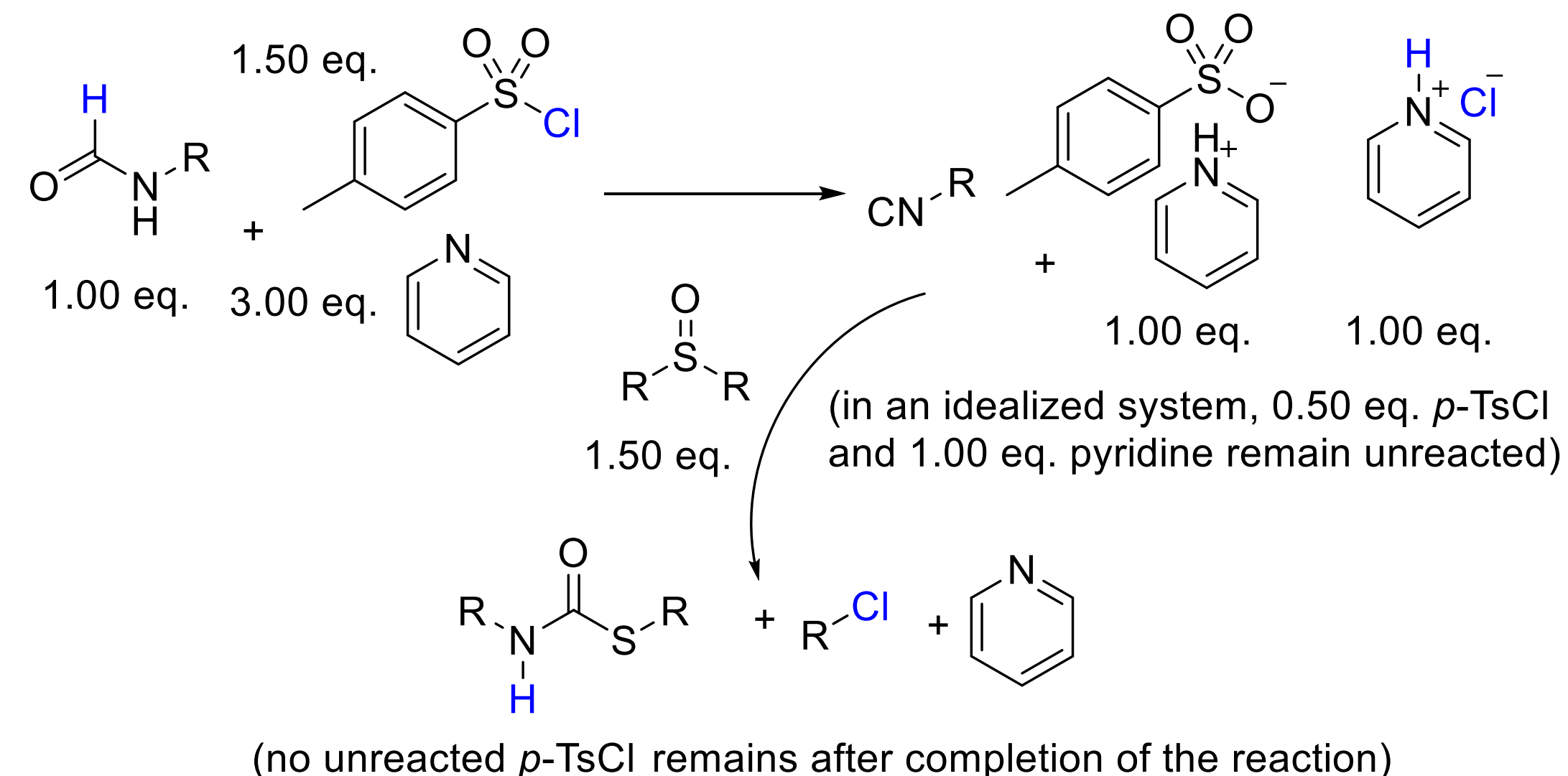
Abstract

An efficient isocyanide-based synthesis of *S*-thiocarbamates was discovered and thoroughly investigated. The new reaction protocol is one-pot and allows the direct conversion of *N*-formamides into thiocarbamates by initial dehydration with *p*-toluene sulfonyl chloride to the respective isocyanide,^[1] and subsequent addition of a sulfoxide component. Contrary to recent literature, which also relies on isocyanides as starting material,^[2–5] in this protocol, no isolation and purification of the isocyanide component is necessary, thus significantly decreasing the environmental and financial impact of the synthesis. The protocol was applied to synthesize a library of sixteen thiocarbamates utilizing four *N*-formamides and four commercially available sulfoxides. Furthermore, experiments were conducted to investigate the reaction mechanism. Finally, four norbornene-based thiocarbamate monomers were prepared and applied in controlled ring-opening metathesis polymerization (ROMP) reactions. The polymers were characterized *via* size-exclusion chromatography (SEC) and their properties were investigated utilizing differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to establish possible applications in material sciences.

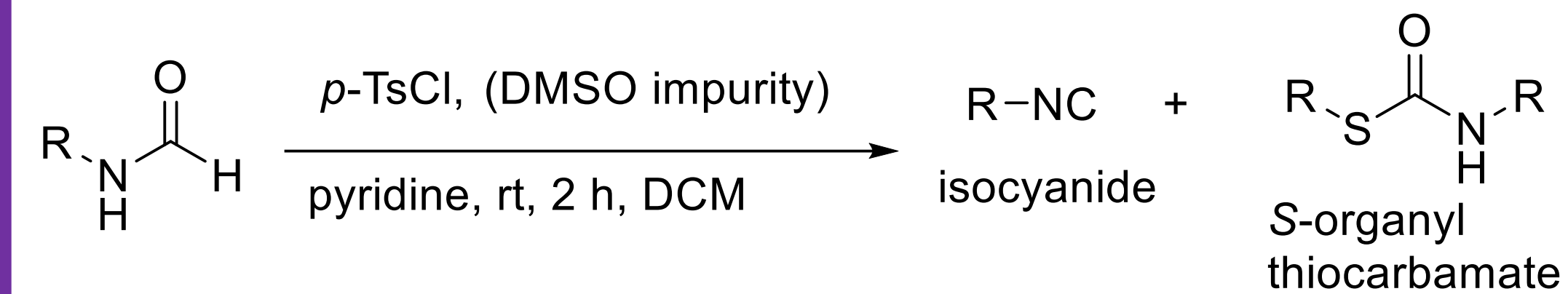
Reaction of benzyl sulfoxide and tetrahydrothiophen-1-oxide



- Benzyl chloride as by-product
- Chloro-thiocarbamates *via* cyclic sulfoxides
- Benzyl sulfide as side-product *via* reduction and possible oxidation of isocyanide

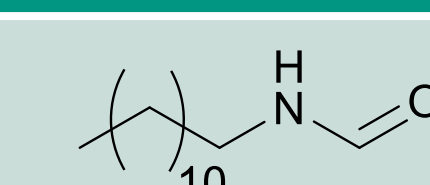
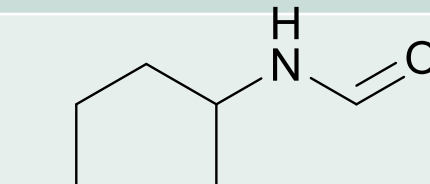
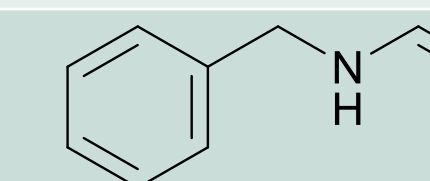
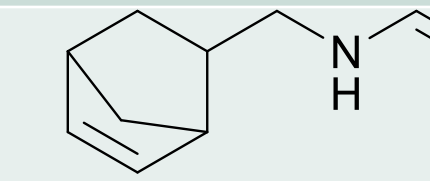


- Formal equivalent of "Py*HCl" necessary for stoichiometry
- *p*-TsCl involved in mechanism as activating agent for the sulfoxide (possibly Swern-like)



- No isocyanide smell
- One pot
- Good yields
- Commercially available sulfoxides
- Activation by *p*-TsCl
- Reductive side reaction
- ROMP
- NMR, SEC, (DSC) and TGA analysis

Table 2. Thiocarbamates synthesized *via* one-pot dehydration and sulfoxide addition.

Entry	<i>N</i> -formamide	Sulfoxide 1	Sulfoxide 2	Sulfoxide 3	Sulfoxide 4
1		77% ^[a]	85% ^[a]	80% ^[a]	53% ^[a]
2		69% ^[a]	70% ^[a]	70% ^[a]	25% ^[a]
3		72% ^[a]	59% ^[a]	81% ^[a]	46% ^[a]
4		60% ^[b]	73% ^[b]	79% ^[b]	50% ^[b]

[a] 1.50 eq. *p*-TsCl, 3.00 eq. pyridine 1M in DCM. 2.50 mmol *N*-formamide. [b] 1.50 eq. *p*-TsCl, 3.00 eq. pyridine 1M in DCM. 10.0 mmol *N*-formamide.

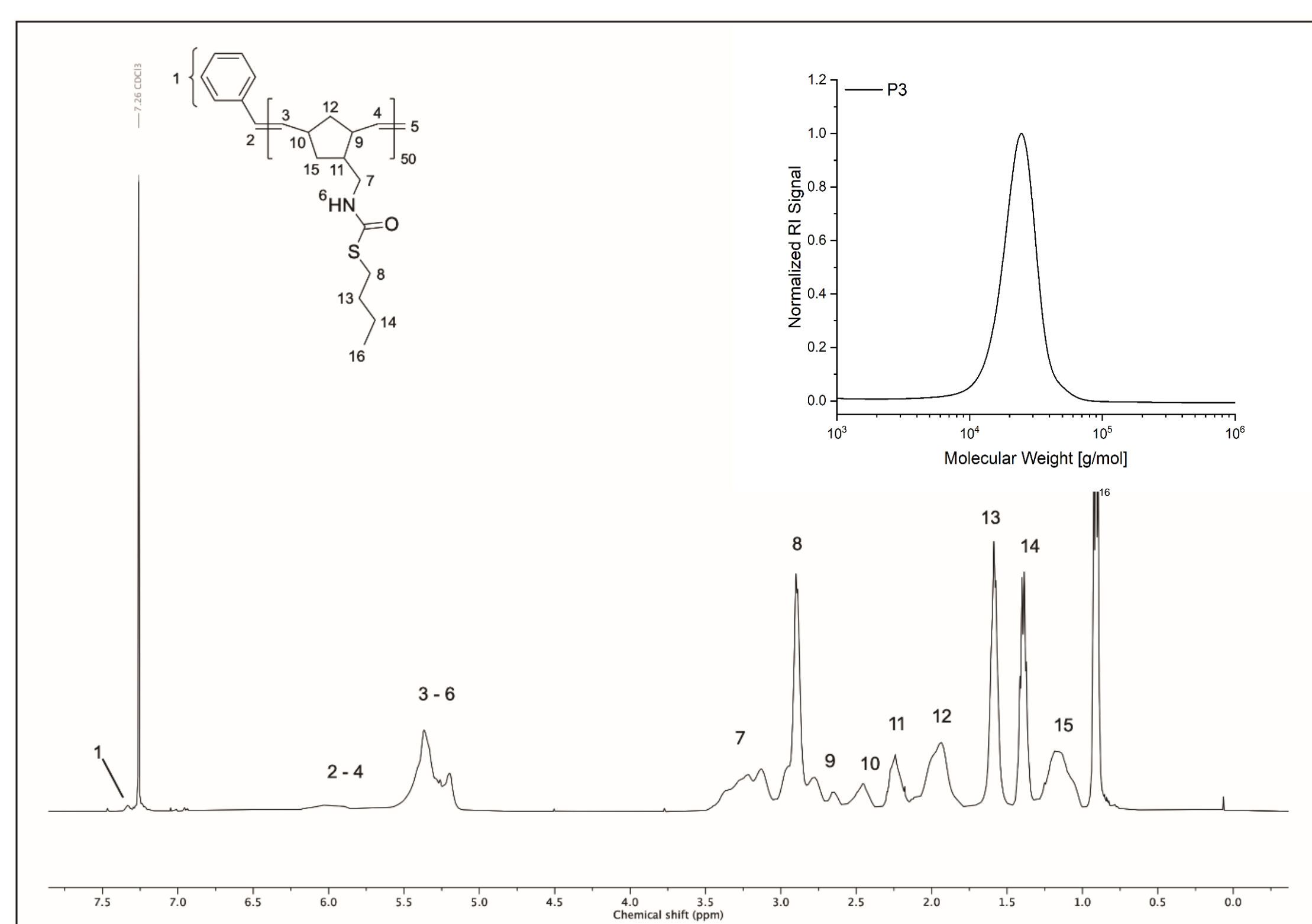


Figure 1. NMR spectrum and SEC graph of polymer P3 (*S*-butyl methyl norbornene thiocarbamate).

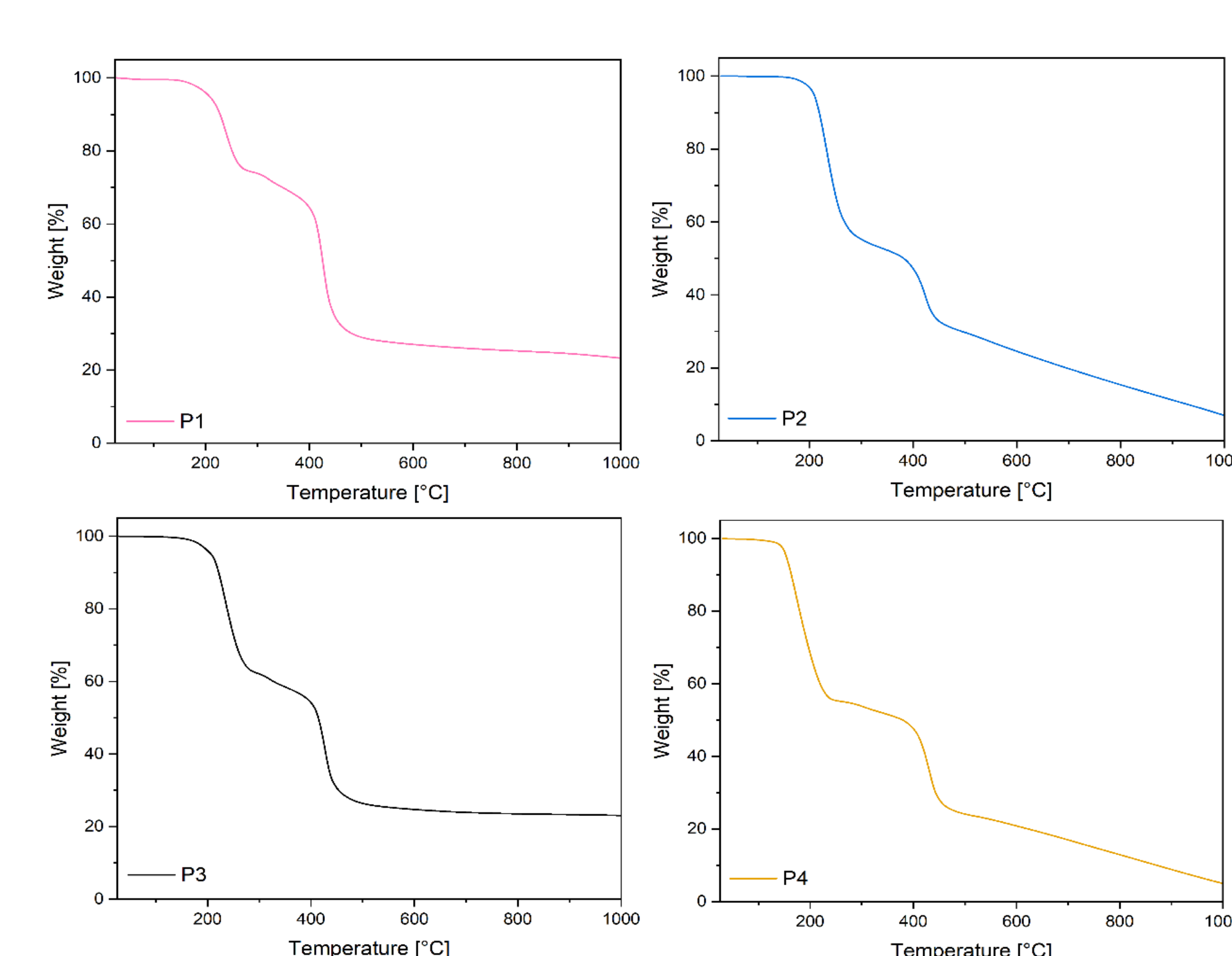


Figure 2. TGA traces of P1-P4. Two distinct degradation points are visible.

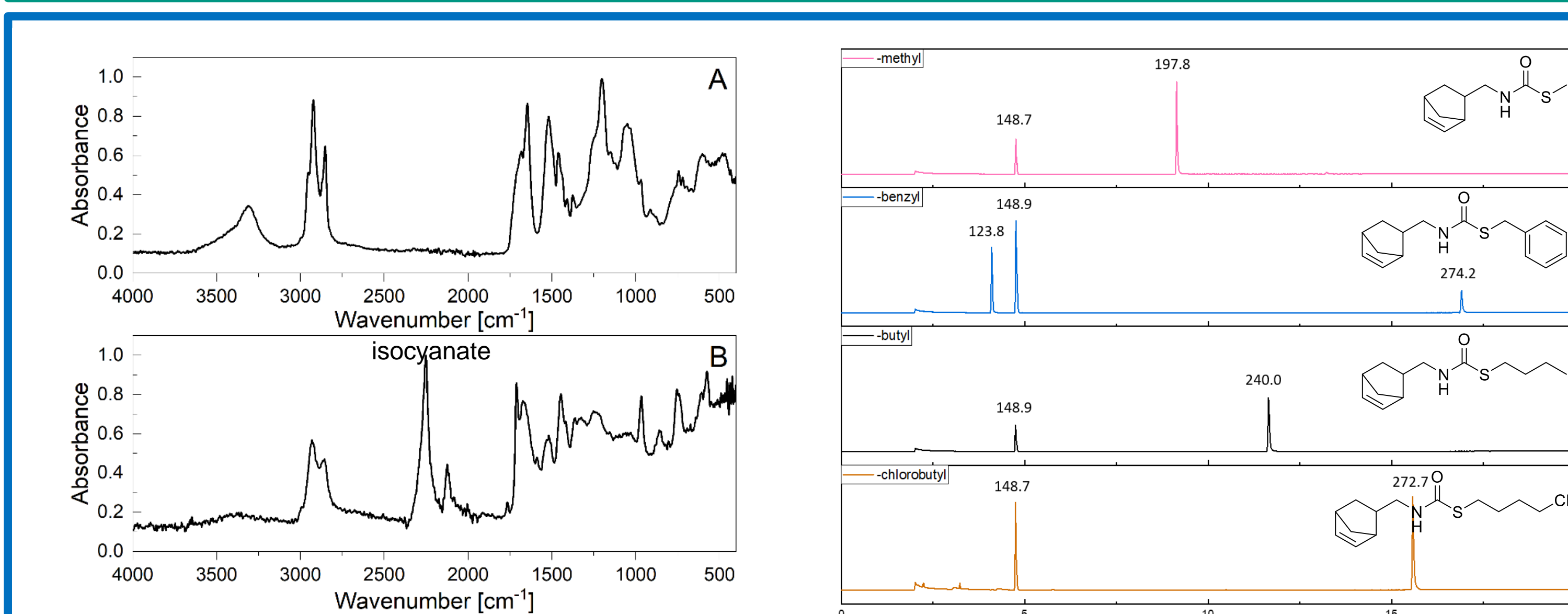


Figure 3. IR spectra of polymer P3 before (A) and after (B) heating at 300 °C for 30 minutes. Bottom spectrum shows clear evidence of an isocyanate moiety.

Figure 4. GC-MS measurements of functionalized norbornene thiocarbamates monitoring thermal decomposition. The signals can be referred to the decomposition products (isocyanate, thiol) and to the initial product.

References

- [1] K. A. Waibel, R. Nickisch, N. Möhl, R. Seim and M. A. R. Meier, *Green Chem.*, **2020**, *22*, 933–941. [2] P. Mampuy, Y. Zhu, S. Sergeev, E. Ruijter, R. V. A. Orru, S. Van Doorslaer, B. U. W. Maes, *Org. Lett.* **2016**, *18*, 2808–2811. [3] S. Wu, X. Lei, E. Fan, Z. Sun, *Org. Lett.* **2018**, *20*, 522–525. [4] Wei, P. Bao, H. Yue, S. Liu, L. Wang, Y. Li, D. Yang, *Org. Lett.* **2018**, *20*, 5291–5295. [5] P. Bao, L. Wang, H. Yue, Y. Shao, J. Wen, D. Yang, X. Zhao, H. Wang, W. Wei, *J. Org. Chem.* **2019**, *84*, 2976–2983.