

ANALYSIS OF SULFONATED POLYESTERS VIA PYROLYSIS-GC/MS AND TGA METHODS

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Introduction

Polyesters belong to the most widely used polymers in the world, their main application being plastic bottles and fibers (polyethylene terephthalate, PET). However, polyesters are very versatile and used for many other (special) applications due to numerous possible variations of suitable monomers. To enhance water compatibility for example, easily solvated functional groups such as sulfonic acids can be introduced into the polymer. For such functionalized polyesters, it is crucial to verify chemical bonding of the sulfonic acids to the polyester and investigate the extend of sulfonation which has been accomplished using thermoanalytical methods.

Experimental

Polyesters were synthesized using neopentyl glycol, isophthalic acid and maleic anhydride in different ratios (degree of unsaturation: 0–60%). The conjugated double bonds were further functionalized with sodium sulfite to reach varying degrees of sulfonation (0–60%). TGA-IR experiments were performed to identify different steps of decomposition to derive correlations with different degrees of sulfonation. Additionally, pyrolysis GC-MS experiments were carried out at 700 °C.

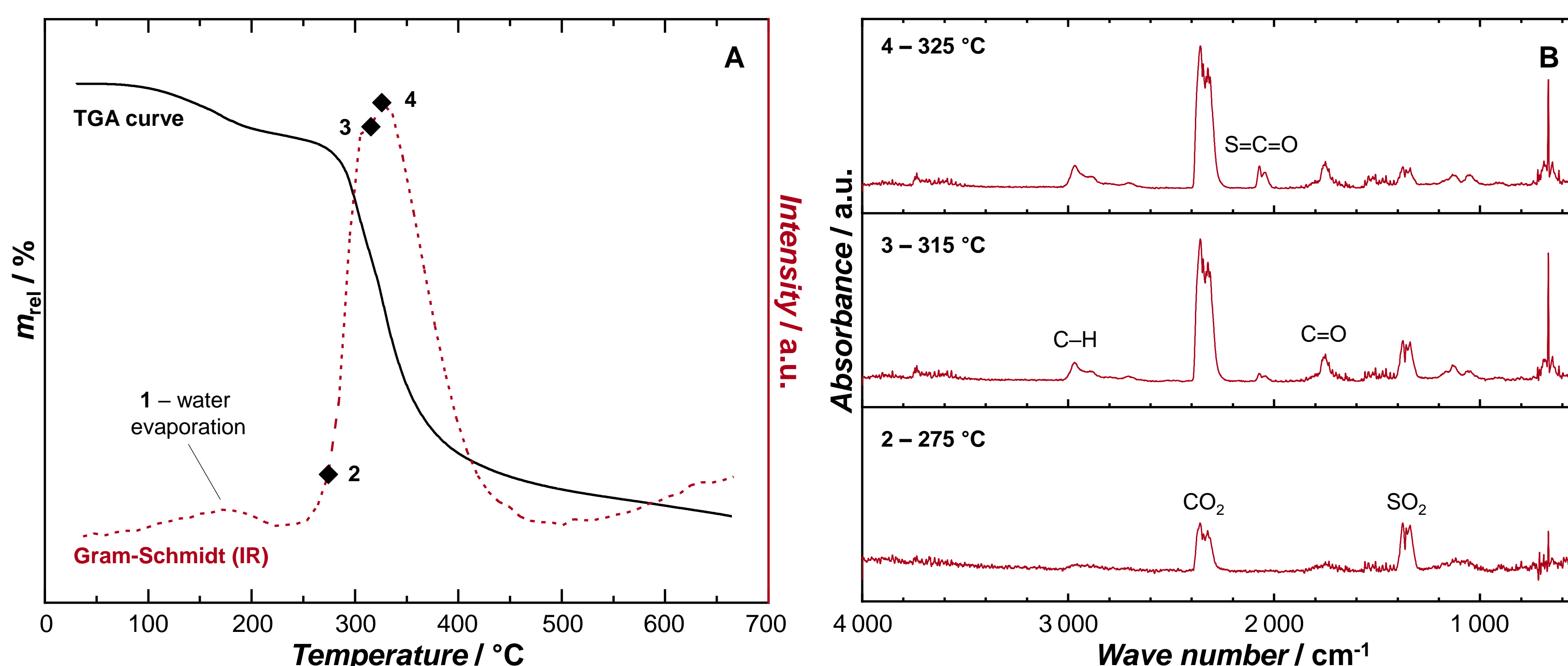


Figure 1: TGA-IR reveals desulfonation of the sulfo-polyesters (SO_2) which mainly overlaps with decarboxylation (CO_2).

Results

TGA-IR gives insights into the decomposition steps of sulfonated polyesters and shows that the elimination of SO_2 and CO_2 overlap (Fig. 1). Thus, a quantification based on the char formation at 540 °C was developed (Fig. 2) and compared to data derived from FTIR spectroscopy (Fig. 3). Whereas the calibration curve shows a nice linear behavior for lower degrees of sulfonation, it underestimates the values of 50 and 60%. Another problem can be seen from Figure 4. The TGA results are strongly dependent on the degree of unsaturation of the original polyester which makes independent cross calibration of TGA results necessary.

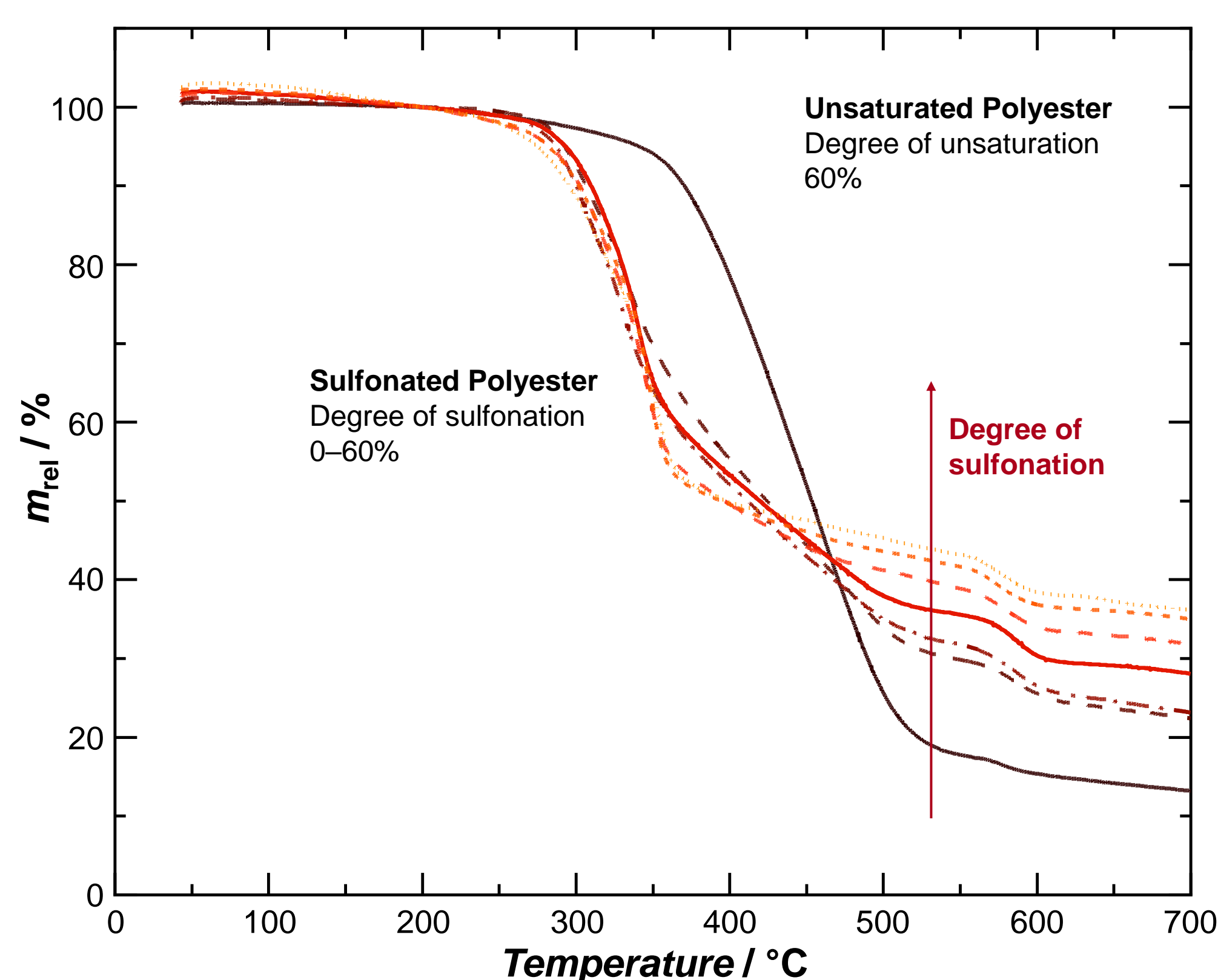


Figure 2: TGA curves of an unsaturated polyester with varying degrees of sulfonation (0–60%) showed trends of decomposition behavior, especially in the range of 540 °C.

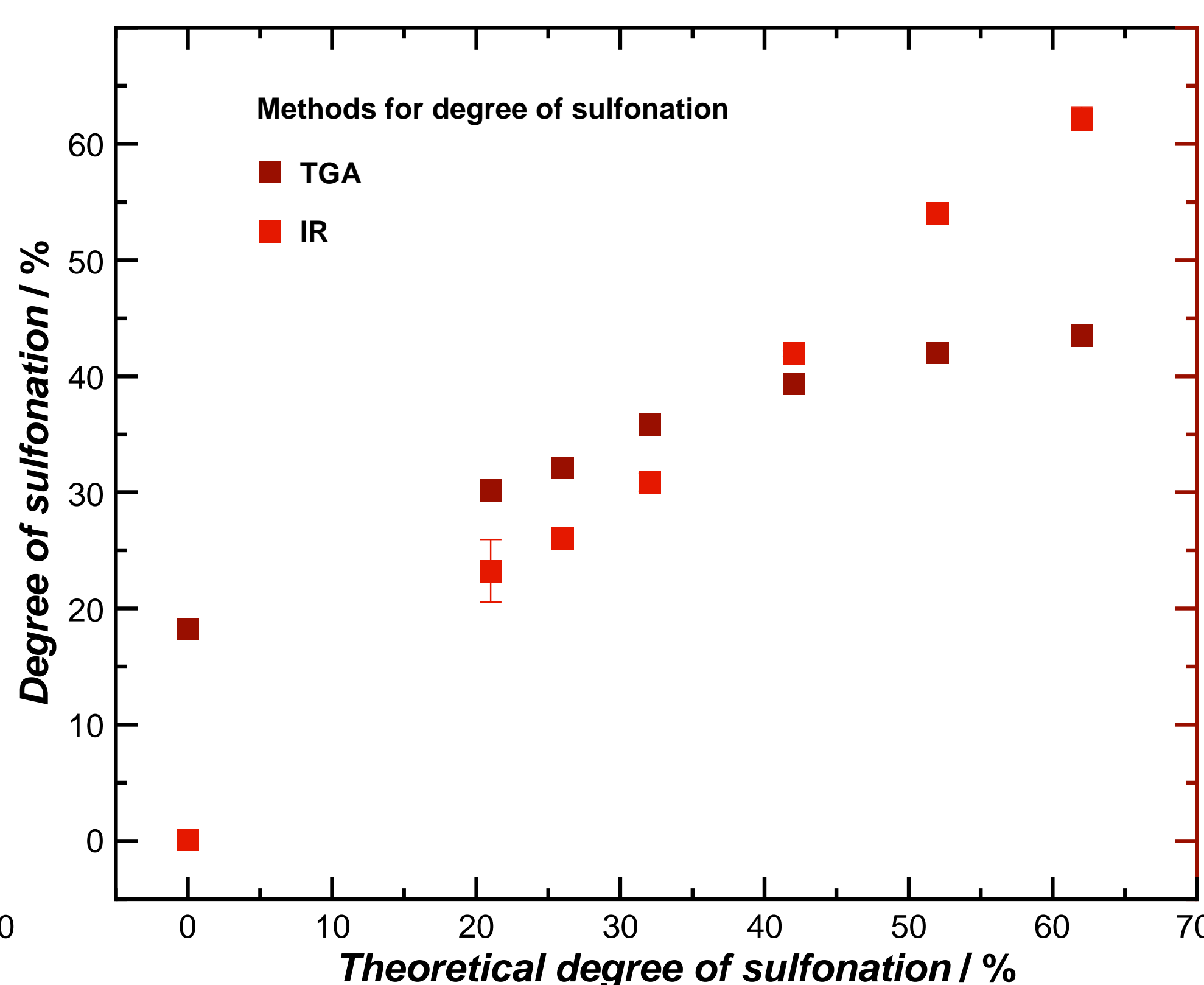


Figure 3: The dependence of the relative mass in TGA (540 °C) on the theoretical degree of sulfonation was compared to results from IR measurements (correlation of S=O to C=O band).

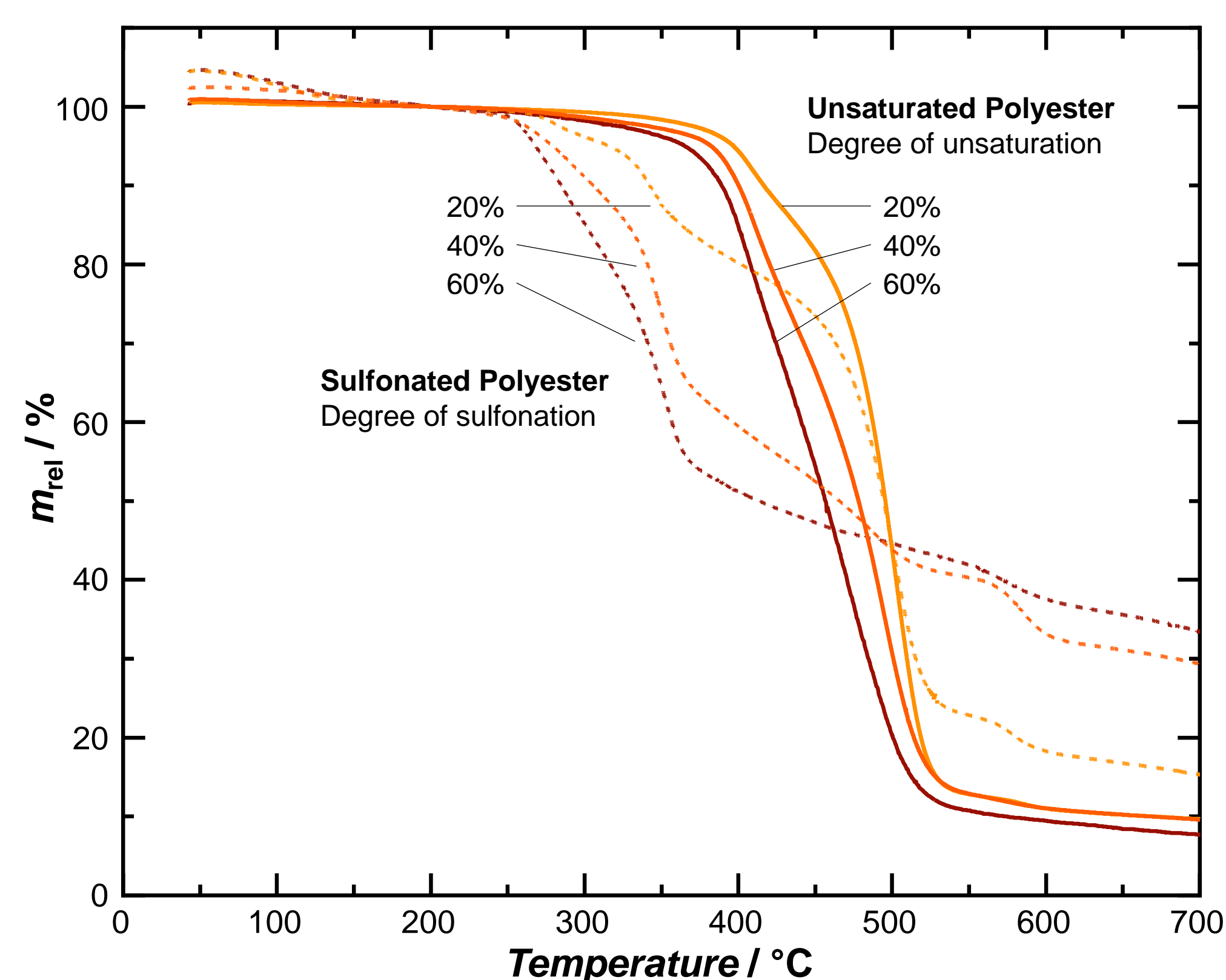


Figure 4: One disadvantage of thermogravimetric analysis for the estimation of the degree of sulfonation was the high dependence on the degree of unsaturation of original polyester.

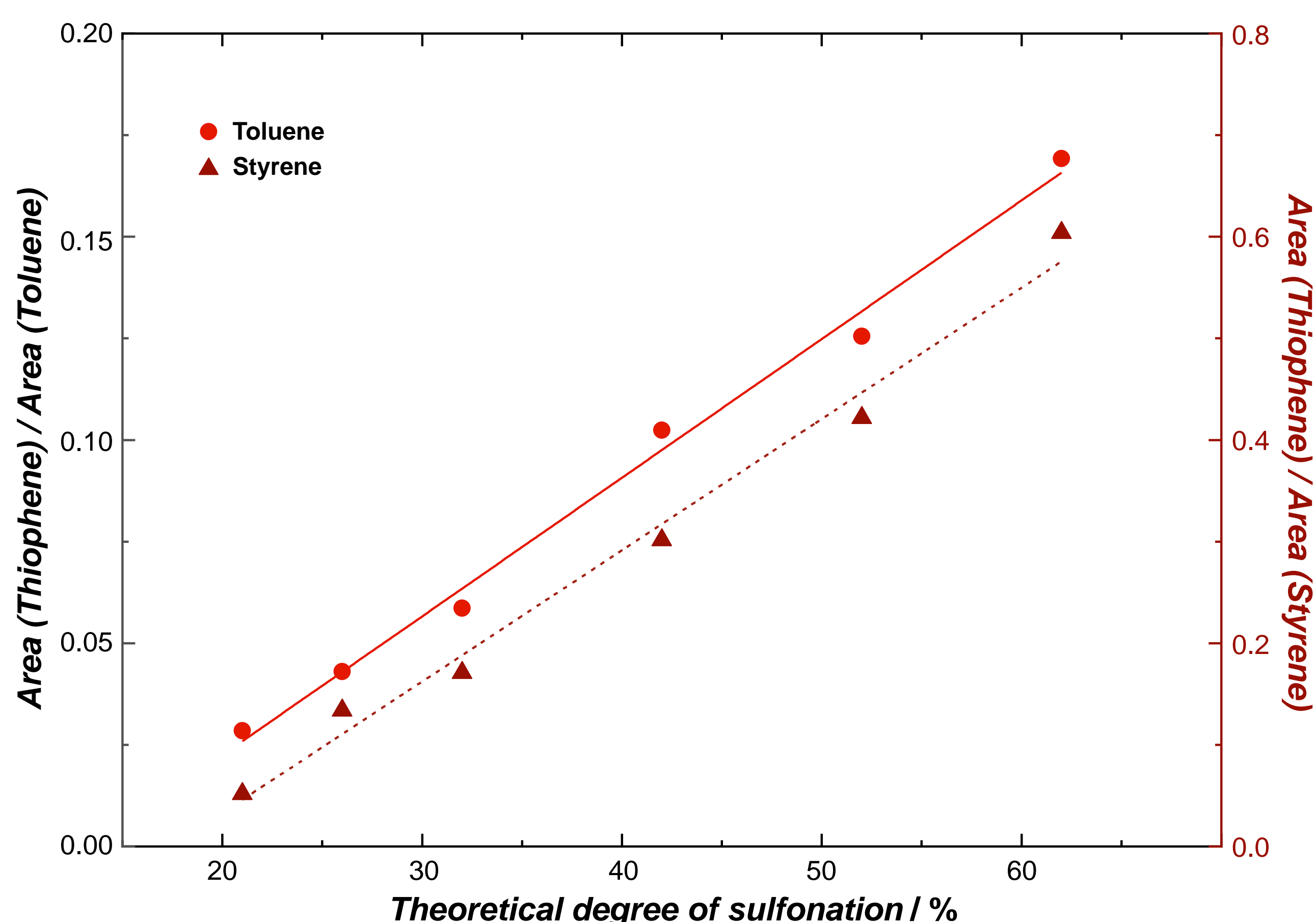


Figure 5: Pyrolysis results showing excellent linearity when thiophene and either toluene or styrene are used as marker compounds.

Pyrolysis at 700 °C results in the formation of several compounds which can be clearly assigned to either the sulfonate group or the polymer backbone. Using both, the ratios of thiophene to toluene or thiophene to styrene as shown in Figure 5 gives calibration curves with excellent linearity. However, when styrene is used as marker for the polyester backbone, the sensitivity is increased by a factor of three.

Conclusion

It could be shown that the determination of the degree of sulfonation in polyesters with thermal methods is possible. Whereas TGA-IR allows a better insight into the thermal decomposition pathways of the material, its use in quantification is not perfect over the complete range of concentrations.

Pyrolysis results in the formation of several breakdown products which are indicative of either the sulfo-group or the polymer backbone. Using the ratios of these compounds has proven to be superior in terms of quantification.