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# Chemical structures assigned for the low molecular weight fractions from degradation of poly(styrene sulfides)

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ABSTRACT

A non-destructive analysis is performed of thermally unstable sulfur–styrene reaction products, combining preparative size exclusion chromatography (P-SEC), ultraviolet–visible (UV–vis) and nuclear magnetic resonance (NMR). The crystallizing compounds are identified as be 2,4-diphenylthiophanes with short sulfur bridge ($x \sim 2$) contrary to earlier suggestions which were based on destructive analysis. A new cyclic structure (styrene polysulfide $x = 1$ up to 8) was assigned to the amorphous species containing a single styrene repeating unit. Comparison with the amorphous fractions suggests that the rigid ring of styrene repeating units in adjacent sequences is the characteristic feature for the crystallisability. The melting and crystallization behaviour of this crystalline component was observed, by optical microscopy (OM) and differential scanning calorimetry (DSC), to be step-wise as well as broad, due to the variation in the length of the sulfur bridge.

## 1. Introduction

Sulfide polymers are used as engineering thermoplastics, sealants and etc. [1] Styrene sulfide oligomer is one of the modifiers used to diminish sulfur blooming both in the rubber industry [2] and sulfur concrete formulation [3]. The styrene sulfide oligomer can be formed at a certain temperature, with some low molecular weight (MW) side products containing not more than two styrene repeating units [4–7]. It is essential to have a clear insight into the chemical structure of each component, since the content and the morphology in the final product may play important roles on the ultimate properties.

Many efforts in the past focused on the chemical structure analysis, but mainly using destructive techniques like mass spectroscopy (MS). An alternating chain structure was suggested for the oligomeric components [5–8], while both cyclic and acyclic structures were assigned for the low MW molecules [5–7,9]. The acyclic low MW molecules were suggested to be alternating chain structures ending with three types of end groups, –SH, $=CH_2$ or $-CH_3$. Part of the low MW side products was found to crystallize during storage at room temperature and the crystalline component was assigned to be 2,4-diphenylthiophene [4,5,7]. From the reported SEC traces of samples withdrawn during the reaction [5], we found the degradation of both the oligomeric and the low molecular species, formed at the early stage of the reaction. 2,4-Diphenylthiophene was one of the degradation products of the very long (200 h) reaction. Its derivative 2,4-diphenylthiophane was detected in some MS analysis [7], but in another study [6] it was reported as an indirect product generated from the acyclic chain structures during destructive MS measurements. Therefore both 2,4-diphenylthiophene and 2,4-diphenylthiophane might not be the original side products.

In a later pyrolysis study [10], thiophene derivatives were detected as a secondary degradation product from poly(styrenedisulfide) and poly(styrenetetrasulfide). Therefore, in the present paper, the emphasis is on the correct identification of the chemical structures of these low MW side products using non-destructive techniques. The product mixture was first fractionated by using P-SEC. One of these fractions was found to crystallize and its melting and crystallization behaviour was followed using OM and DSC. The chemical structures were analyzed using UV and NMR methods, to identify the length of the sulfur bridge ($x$) and the sequence of the sulfur and styrene repeating units respectively. The crystallisability of the crystalline components is discussed in terms of their chemical structures.

## 2. Experimental section

### 2.1. Synthesis of MBS

Sulfur (99.99%, Shell) (10 g) was preheated to 135 °C until completely molten. Styrene (99.9%, Sigma–Aldrich) (15 g) was then

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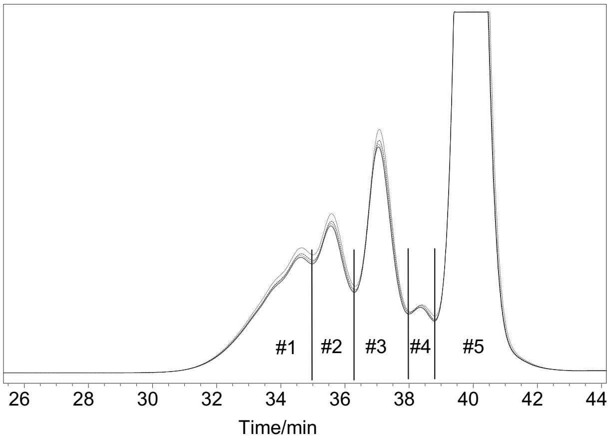

**Fig. 1.** P-SEC traces (at 254 nm) of the crude product mixture. Five fractions, #1 to #5, were collected for further analysis.

**Table 1**
The approximated number ($n$) of styrene repeating units, at the peak position of each fraction.

| Fractions | #1 | #2 | #3 | #4 | #5 |
|---|---|---|---|---|---|
| $n$ | $\geq 4$ | $\leq 4$ | $\geq 2$ | $=2$ | 1 |

added to the liquid sulfur at a weight ratio of 3:2. The mixture was heated at 135 °C for 1 h. Tetrahydrofuran (THF) (50 mL) was added to the reactor to extract the styrene sulfide oligomers and the low MW compounds from sulfur. Both THF and unreacted styrene were then evaporated to obtain the crude product.

### 2.2. *Sample preparation*

The crude mixture was dissolved in THF at a concentration of 10 mg/mL. Fractionation using P-SEC was carried out on a Waters GPC equipped with a Waters 490 pump, a Linear UV–VIS 200 detector (at 254 nm), a Waters WISP 712 auto injector (250 µL injection volume), a PSS SDV (10 µm particles) 300 mm × 20 mm column (20 °C) and a Gilson fraction collector with 44 positions. THF (Biosolve) was used as eluent at a flow rate of 1.75 mL/min. The calibration was done using polystyrene standard samples (Polymer Laboratories, 580 to $7.1 \times 10^6$ g/mol). Five fractions of the sample were obtained. These fractions were dried in a vacuum oven at 30 °C for three days, then dissolved in deuterated chloroform ($CDCl_3$) and filtered before NMR measurements. A droplet of the NMR sample was cast onto a potassium bromide substrate or a quartz plate, and dried for OM or UV–vis Spectroscopy.

### 2.3. *Characterization methods*

The morphology of each fraction was studied on an Axioplan optical microscope coupled with Linkam hot stage. The images were recorded at a 40× magnification using bright field transmission mode with and without a cross-polarizer.

The UV–vis spectra were recorded on an HP8453 UV–vis spectrometer.

$^1$H NMR and g-COSY spectra (400 MHz) were recorded on a Varian Mercury Vx400 spectrometer. g-HMQC spectrum was recorded on a 500 MHz NMR device.

## 3. Results and discussion

### 3.1. *Fractionation of the product mixture*

The reaction product mixture was fractionated using a P-SEC, monitored with a UV–vis detector at 254 nm, as shown in Fig. 1. The crude product solution was injected four times. The reproducibility is shown by the overlay of the SEC traces. Five fractions #1 to #5 were collected, as indicated in Fig. 1.

Since the P-SEC column was calibrated using polystyrene standards, only a relative MW can be estimated. The approximated number of styrene repeating units ($n$) at the peak position of each fraction is listed in Table 1. The relative MW of fraction #4 is expected to be higher than that of fraction #5, due to its slightly shorter elution time. Therefore $n$ is estimated to be 2 and 1 for fraction #4 and #5 respectively.

### 3.2. *Morphology comparison between different fractions*

The optical microscopy images of each fraction are displayed in Fig. 2. Interestingly, only one of the low MW fractions, fraction #4, was found to crystallize, while all the other fractions appeared to be amorphous.

### 3.3. *Melting and crystallization behaviours of fraction #4*

In some previous studies, the crystalline products of styrene and sulfur reactions were suggested to consist of 2,4-diphenylthiophene.

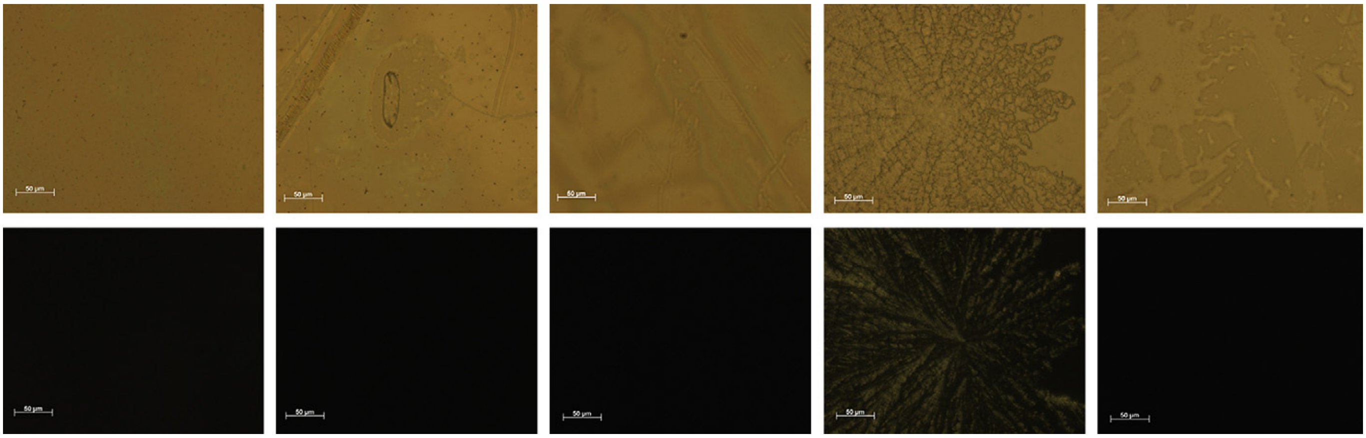

**Fig. 2.** Images of fraction #1 to #5 (from the left to the right), captured in bright field without (in the first row) and with (in the second row) a cross-polarizer. The scale bars represent 50 µm.