Colloid Polym Sci 273:648–652 (1995)

ORIGINAL CONTRIBUTION

K. Ganesh
K. Kishore

Studies on model oligosulfides to understand polysulfide polymers

Received: 17 October 1994
Accepted: 14 February 1995

Dr. K. Ganesh (✉) · K. Kishore
Department of Inorganic and Physical Chemistry
Indian Institute of Science
560025 Bangalore, India

Abstract 1-bromo-1-phenylethane was reacted with aqueous sodium disulfide or sodium tetrasulfide to form the 1-phenylethyl polysulfides of sulfur rank 2 or 4 respectively. The distribution of the 1-phenylethyl polysulfides thus formed was studied using ^{1}H NMR and GC-MS analysis. Apart from 1-phenylethyl disulfide and 1-phenylethyl tetrasulfide being produced in large amounts when aqueous sodium disulfide and sodium tetrasulfide were used respectively, the formation of 1-phenylethyl monosulfide in the former case and both mono and disulfide in the latter case, in minor amounts, is also observed. Also, it was found that the undetection of the molecular ion peaks of 1-phenylethyl polysulfides having rank above 2 is due to their thermal decomposition to elemental sulfur, 1-phenylethyl mono and disulfide, under the heating conditions employed for GC-MS analysis.

Key words Aqueous sodium disulfide – aqueous sodium tetrasulfide – sulfur rank-1-phenylethyl polysulfide – total ion chromatogram (TIC)

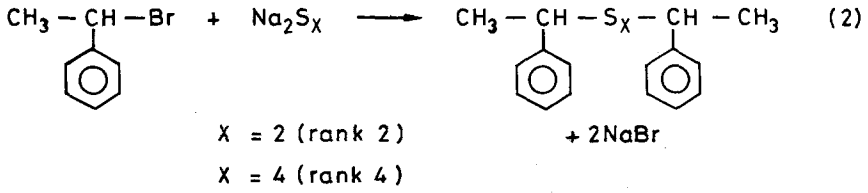
Introduction

Because of their versatile applications, such as adhesives, insulators, coatings, etc., studies on polysulfide polymers have assumed great importance [1]. Industrially, polysulfide polymers are made by the step growth polymerization of organic dihalide with aqueous sodium polysulfide (Eq. (1)),

$$\text{Cl–R–Cl} + \text{Na}_2\text{S}_x \longrightarrow \text{–(–R–S}_x\text{–)}_n\text{–} + 2\text{NaCl}\,, \qquad (1)$$

where "x" is referred to as the rank and represents the average number of sulfur atoms present in the polysulfide unit. The widely used polysulfide polymers either have rank 2 or 4 [1]. Since aqueous sodium polysulfide contains a distribution of sulfide anions ranging S^{2-} to S_5^{2-} and possibly higher, the term "sulfur rank" merely represents the average number of anions present [1]. Due to this the polymer obtained will generally contain a distribution of sulfide linkages ranging from mono to penta. Since the ultimate property of a polysulfide polymer depends essentially on the type of linkages it possess, its precise knowledge (identification and concentration) in the sample using spectroscopic techniques is very much desirable, but it is greatly hampered due to their insolubility in common organic solvents [2]. We have attempted here to investigate the distribution of polysulfide linkages by making soluble simple organic polysulfide as a model to mimic the polysulfide polymers. The polymer analogous reaction studied here is the condensation of 1-bromo-1-phenylethane either with aqueous sodium disulfide (aq.Na_2S_2) or

with aqueous sodium tetrasulfide (aq.Na_2S_4) (Eq. (2)).



Experimental

The ^1H NMR spectra were recorded on a Bruker AC 200F NMR spectrometer as solutions in $CDCl_3$ with TMS as the internal standard.

The GC-MS analysis has been carried out in a Jeol-JMX-DX-303-GC-Mass spectrometer. The conditions employed were: Carbovax OV capillary column; injector temperature 250 °C; separator temperature 230 °C; inlet temperature 200 °C; column was heated from 100–250 °C at a rate of 4 °C/min and chloroform was used as the solvent.

Synthesis of bis(1-phenylethyl) polysulfide (rank 2)

The starting material, 1-bromo-1-phenylethane was prepared using the reported procedure [3]. One mole of 1-bromo-1-phenylethane in chloroform was added to 2 mols of aq.Na_2S_2 [4] followed by the addition of tetrabutylammonium bromide as a phase transfer catalyst. The mixture was stirred at room temperature for 24 h. The chloroform layer was separated, washed several times with water and dried over anhydrous sodium sulfate. The chloroform solution was then evaporated to get bis(1-phenylethyl) polysulfide of rank 2.

A similar procedure was adopted for preparing the rank 4 polysulfide also by condensing 1-bromo-1-phenylethane with aq.Na_2S_4. The procedure for making the aq.Na_2S_4 was followed using the literature procedure [5].

Results and discussion

1-phenylethyl polysulfide (rank 2)

The ^1H NMR spectrum of the 1-phenylethyl polysulfide (rank 2) is displayed in Fig. 1. The peak at 7.1–7.6 ppm corresponds to the phenyl ring protons absorption. While the methyl protons is found to absorb between 1.4–1.6 ppm, on the other hand, the methine proton exhibited a broad absorption with multiplets in the range of 3.2–4.4 ppm. The broad peak of the methine proton is very

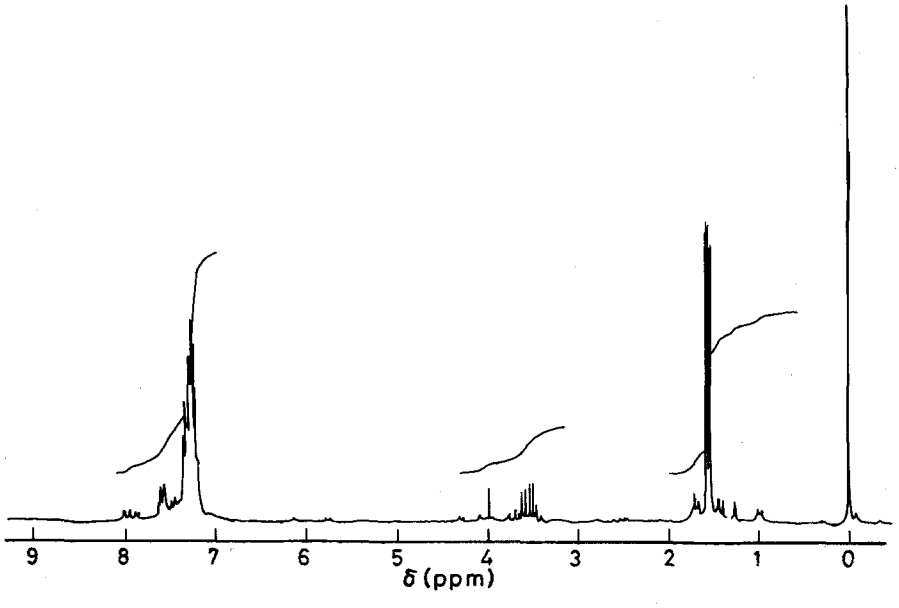


Fig. 1 ^1H NMR spectrum of 1-phenylethyl polysulfide (rank 2)

interesting and reveals some insight into the formation of higher rank sulfides namely, tri, tetra and penta. It was reported earlier that the methine proton of pure 1-phenylethyl disulfide absorbs at 3.5 ppm and that of the trisulfide at 4.1 ppm [6]. Comparison of the literature data with Fig. 1. clearly exhibits that the disulfide is formed in larger concentrations since the multiplet observed at 3.5 ppm has a higher intensity. But the presence of weak broad absorption beyond 3.5 ppm (3.5–4.4 ppm) also confirms the formation of higher sulfide like tri, tetra and penta to minor levels.

The total ion chromatogram (TIC) as well as the mass spectrum corresponding to the individual peak maxima's in the TIC of 1-phenylethyl polysulfide (rank 2) are presented in Figs. 2 and 3 respectively. The largest peak in the TIC (Fig. 2d) and its corresponding mass spectrum (Fig. 3d) reveals that the maximum mass peak is observed to be 274 m/z which is the molecular ion peak of 1-phenylethyl disulfide. Hence it is clear that the disulfide is produced in larger amounts when aq.Na_2S_2 is used. Besides, the presence of monosulfide, i.e., 1-phenylethyl sulfide (mol. wt. 242), in the mixture is also confirmed (refer Fig. 2a and 2b; Fig. 3a and 3b). Although the ^1H NMR spectrum (Fig. 1) exhibited the presence of higher sulfides, their absence in the GC-MS analysis is presumably due to their very low concentrations and hence could not be detected from the latter analysis.

1-phenylethyl polysulfide (rank 4)

The ^1H NMR spectrum of the 1-phenylethyl polysulfide (rank 4) is presented in Fig. 4. The phenyl ring protons were found to be absorbed between 7.0–7.6 ppm. The

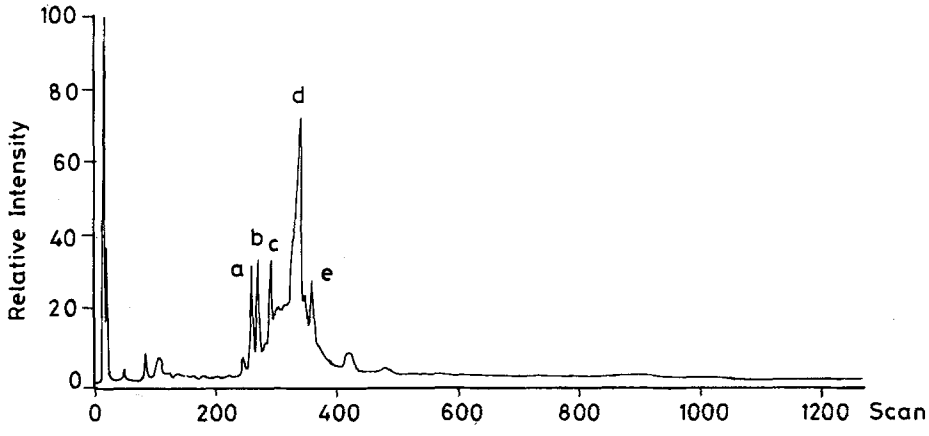


Fig. 2 TIC of 1-phenylethyl polysulfide (rank 2)

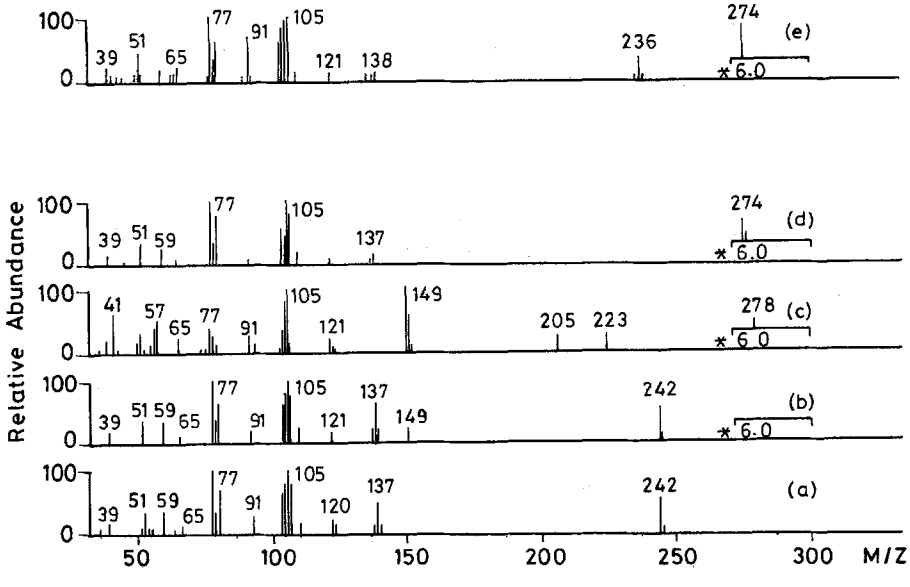


Fig. 3 Mass spectra corresponding to individual peak maxima of Fig. 2

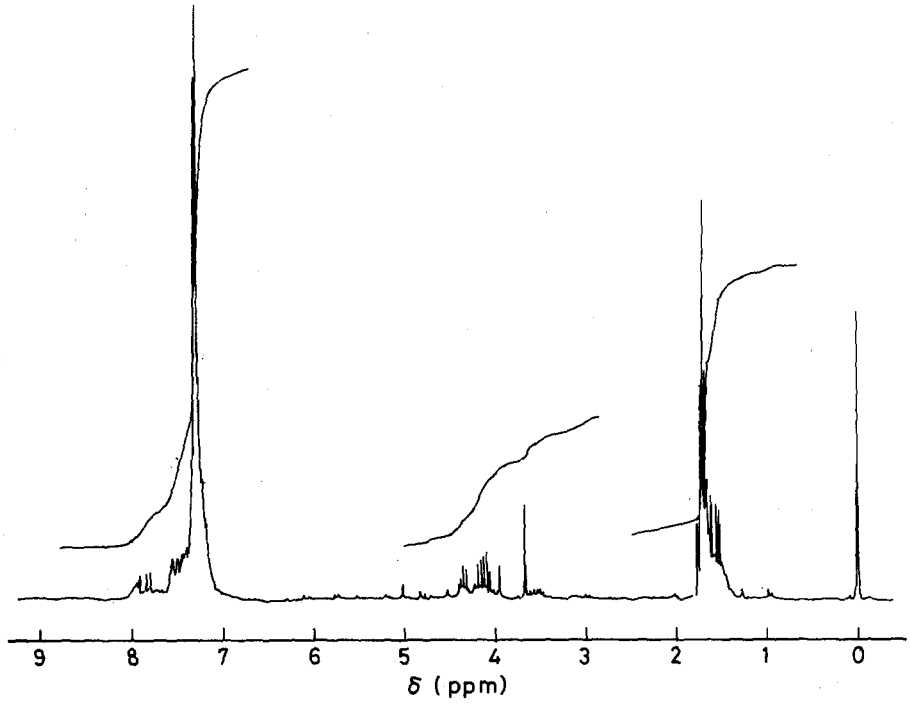


Fig. 4 ^{1}H NMR spectrum of 1-phenylethyl polysulfide (rank 4)

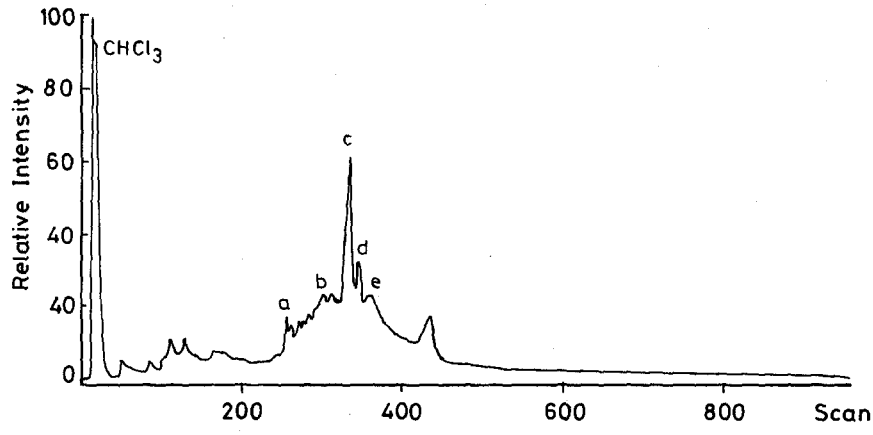


Fig. 5 TIC of 1-phenylethyl polysulfide (rank 4)

peaks between 1.3–1.8 ppm and 3.4–4.8 ppm are attributed to the methyl protons and methine proton absorption respectively. From the chemical shift values of the methine proton of neat 1-phenylethyl disulfide and 1-phenylethyl trisulfide, it is clear that with the increase in the rank, the methine proton absorption tends to undergo a downfield shift. Also, it may be expected that a further downfield shift of the methine proton absorption with increase of sulfur rank, i.e. tetra, penta, etc. will be negligible. Hence, strong absorption at the 4.1 ppm, in Fig. 4, is assigned to the methine proton absorption of the 1-phenylethyl tetrasulfide. It may be noted here that multiplets of low intensity in the region of 3.5 ppm corresponds to the methine proton absorption of the 1-phenylethyl disulfide and hence its presence in the mixture, in small amounts, is also confirmed.

The TIC and the mass spectrum corresponding to the individual peak maxima's of the 1-phenylethyl polysulfide (rank 4) is shown in Figs. 5 and 6 respectively. From the mass spectra only the molecular ion peaks of the disulfide (274 m/z; Fig. 6c and 6e) and that of monosulfide (242 m/z; Fig. 6a) is observed. But the ^{1}H NMR spectrum of the same mixture (Fig. 4) revealed the formation of the 1-phenylethyl tetrasulfide in larger amounts. The absence of the molecular ion peaks for tri, tetra and penta could be due to the thermal decomposition of these sulfides to 1-phenylethyl disulfide and 1-phenylethyl monosulfide with the evolution of elemental sulfur (Eq. (3)), under the

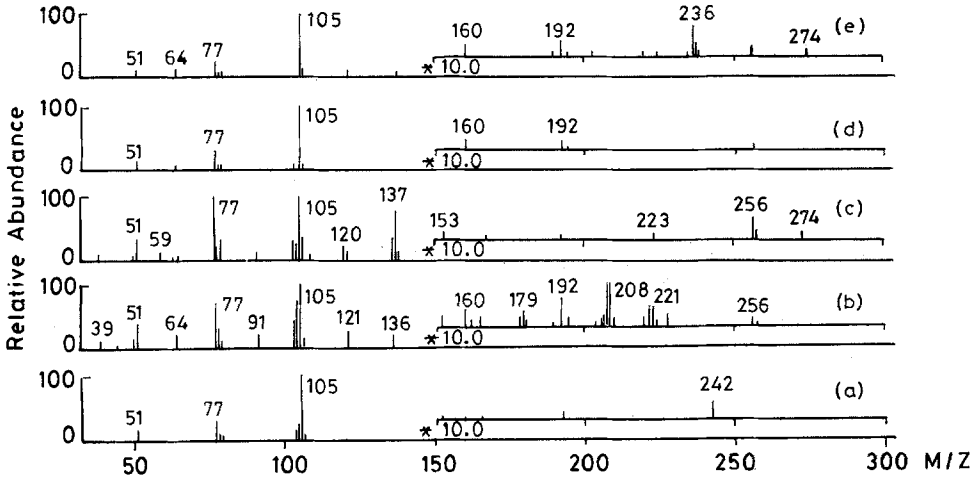
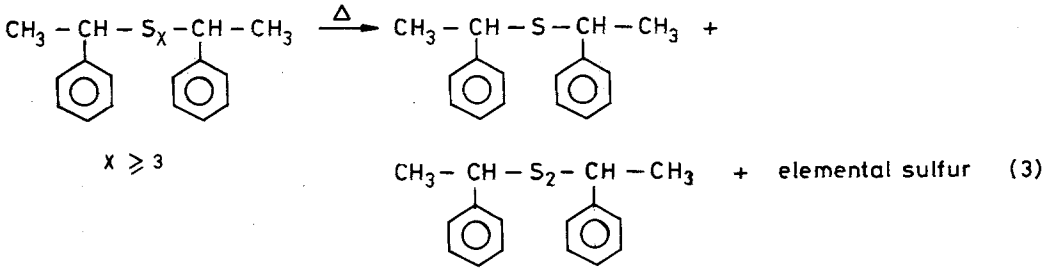


Fig. 6 Mass spectra corresponding to individual peak maxima of Fig. 5



heating conditions employed in the GC-MS. This is confirmed from the fact that the elemental sulfur peaks (S_2 64 m/z; S_5 160 m/z; S_6 192 m/z and S_8 256 m/z) are clearly seen in the Fig. 6b, 6c, 6d and 6e.

References

1. Gobran RH, Berenbaum MB (1969) In: High Polymers Vol. XXIII, Kennedy JP, Tornquist EGM, Eds, Interscience, New York
2. Kishore K, Ganesh K (1995) Adv Polym Sci 121:81
3. Popielarz R, Arnold DR (1990) J Am Chem Soc 112:3068
4. Kishore K, Ganesh K (1993) Macromolecules 26:4700
5. Sander SR, Karo W (1980) In: Organic Chemistry: A series of monographs, Academic, New York
6. Harpp DN, Smith RA (1982) J Am Chem Soc 104:6045