## 4.2   Synthesis and Characterization of the Sulfur-Oligomeric Alkenyl Polysulfide (OAPS) Copolymeric System:

It has been found that alkyl polysulfides dissolve very readily in liquid sulfur at 140°C. Diallyl monosulfide has been reported to copolymerize with liquid sulfur[23]. These observations lead to the synthesis of oligomeric alkenyl polysulfide (OAPS) so as to investigate its network forming copolymerization reaction with liquid sulfur and structure-property studies on the copolymeric materials.

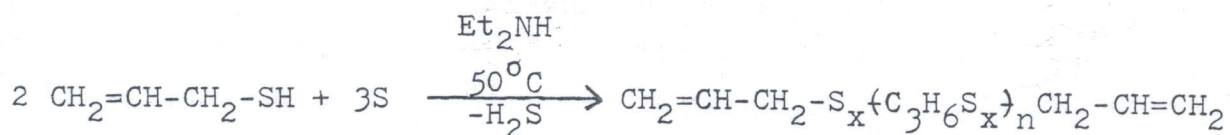### 4.2.1.   Synthesis of Oligomeric Alkenyl Polysulfide (OAPS) From Allyl Thiol and Sulfur Using a Basic Catalyst:

The reaction of thiols with sulfur in the temperature range 130°-160°C to form polysulfides, RS_xR/ArS_xAr, where x is the rank of sulfur, has been investigated in some detail[48,49]. A free radical mechanism has been proposed for the reaction[49]. Also it has been reported that the reaction is base-catalyzed, probably by a general base-catalyzed path obeying the Bronsted law[48]. In the presence of an amine catalyst, the reaction has been reported to go even at ambient temperature[11,50]. Diethyl amine has been found to be a very effective catalyst in the present study in the temperature range of about 20-50°C.

The base catalyzed reaction of 2 moles of dodecyl thiol with 3 g-atoms of sulfur:

$$2\ C_{12}H_{25}SH + 3\ S \xrightarrow[50°C]{Et_2NH} C_{12}H_{25}S_xH_{25}C_{12} + H_2S$$

$$(\overline{x} = 4)$$
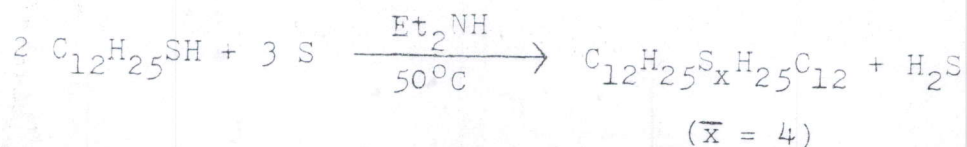
gives 1 mole of dodecyl polysulfide of average sulfur rank ($\bar{x}$) 4 .(Calc. for tetrasulfide, MW = 466.5, 61.79% C. 10.72% H and 27.49% S; Obs. MW = 470 (vapor pressure osmometry), 62.42% C, 10.75% H and 26.42% S).

However, the base catalyzed reaction of 2 moles of allyl thiol with 3 g-atoms of sulfur:

$$2 \ CH_2=CH-CH_2-SH + 3S \ \xrightarrow[\substack{-H_2S}]{\substack{Et_2NH \\ 50^\circ C}} \ CH_2=CH-CH_2-S_x\{C_3H_6S_x\}_n CH_2-CH=CH_2$$

gives a distribution of oligomeric polysulfides with the average degree of oligomerization equal to n. If the polysulfide was only diallyl polysulfide of average sulfur rank 4, the molecular weight would have been expected to be 210.3. But molecular weights of about 280-350 (perhaps even higher) are obtained. These molecular weights do not appear to be reproducible. The color of the polysulfide changes from yellow to red as the amount of Et_2NH for its synthesis is increased, but no significant effect on molecular weight is observed. The purity of sulfur (e.g., 99.9995% or 99.8%) does not appear to have any significant effect on molecular weight either. The following reasons have been cited for the irreproducibility of the molecular weight of the polysulfide:

1. The allyl thiol contains a double bond which is an additional site for addition reactions with thiol in the presence of a basic catalyst[51].

2. It is a heterogeneous reaction of solid sulfur with a liquid thiol where sulfur goes into solution by the formation of polysulfide. There-

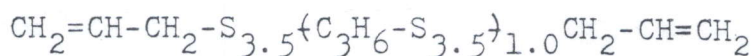fore, the reaction is expected to be dependent on the efficiency of the mechanical mixing of the system.

3. Allyl thiol appears very much more reactive than alkyl thiols, because very slow evolution of H_2S is observed at $50^{\circ}C$ even without the addition of Et_2NH, particularly when the sulfur is very pure (e.g., 99.9995%). The span of time before the addition of Et_2NH to the thiol-sulfur system appears qualitatively to affect the molecular weight, perhaps the longer the time, the higher the molecular weight of polysulfide.

The formulae for two samples of OAPS, which are obtained by the reaction of 2 moles of allyl thiol with 3 g-atoms of sulfur, are determined from their molecular weights (number-average) and elemental analyses and are shown below:

OAPS-280 : MW = 280, 30.51% C, 4.52% H and 64.77% S

$$CH_2=CH-CH_2-S_{4.0}(C_3H_6-S_{4.0})_{0.4}CH_2-CH=CH_2$$
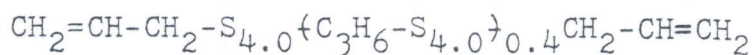
OAPS-350 : MW = 350, 31.08% C, 4.58% H and 64.42% S

$$CH_2=CH-CH_2-S_{3.5}(C_3H_6-S_{3.5})_{1.0}CH_2-CH=CH_2$$

The values of n shown above are only the average numbers. Chemical ionization mass spectrometric studies have been carried out on a sample of OAPS-350, where n is 1.0, using iso-butane as the reactant in order to obtain a mass spectrum without much fragmentation. In chemical ionization mass spectrometry, usually the spectra contain significant amount ions with m/e values equal to one unit higher than the molecular weights of the compounds[52]. Hence it is relatively simple to detect the species of varying molecular weights in

the oligomeric distribution of polysulfides by chemical
ionization mass spectrometry. Only the diallyl polysulfides
(where n = 0) have been observed. The higher oligomers are
not observed due to their extensive decomposition at the high
operating temperature of $240^{\circ}C$. (See Appendix II for details.)
However, it (i.e., the presence of n = 0 in a sample of n = 1)
gives sufficient evidence to indicate that an oligomeric
distribution of polysulfide does exist. The relative
composition of some diallyl polysulfides:

$$CH_2=CH-CH_2-S_x-CH_2-CH=CH_2,$$
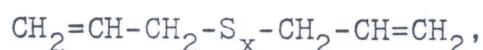
are observed to be 100.0%, 64.3% and 22.7% for x = 2, 1 and 3,
respectively. It is, however, possible that interconversion
between different diallyl polysulfides may have occurred by
redistribution reactions[53].

4.2.1.1. Structure Characterization and
Determination of the "Polysulfide
Distribution" in Oligomeric Alkenyl
Polysulfide (OAPS) by NMR Analysis:

The NMR spectrum (in CS_2) of diallyl sulfide (Figure 14)
shows two groups of protons, A and B, for the olefinic and the
allylic protons, respectively. The NMR spectra (in CS_2) of
OAPS-280 and OAPS-350 (Figures 15 and 16) show three distinct
groups of proton - A, B and C. The signals in the region C
(Figures 15 and 16) are attributed to the saturated protons of
OAPS; the effect of molecular weight of OAPS, which in turn
affects the intensity of the signals in the region C, is
clearly observed in the spectra. The chemical shifts of two model

Table 10

Chemical Shifts (δ) of the α-Hydrogens in Diethyl
Polysulfide and Diallyl Polysulfide (RS_xR) in CS_2
with TMS as the Internal Standard

R	x=1	x=2	x=3	x=4	$\Delta\delta_{2-1}$	$\Delta\delta_{3-2}$	$\Delta\delta_{4-3}$
CH_3-CH_2-	2.43[a]	2.62	2.82	2.92	0.19	0.20	0.12
$CH_2=CH-CH_2-$	2.98[b]	3.26	3.43	3.52	0.28	0.17	0.09

(a) - in CCl_4 [57]
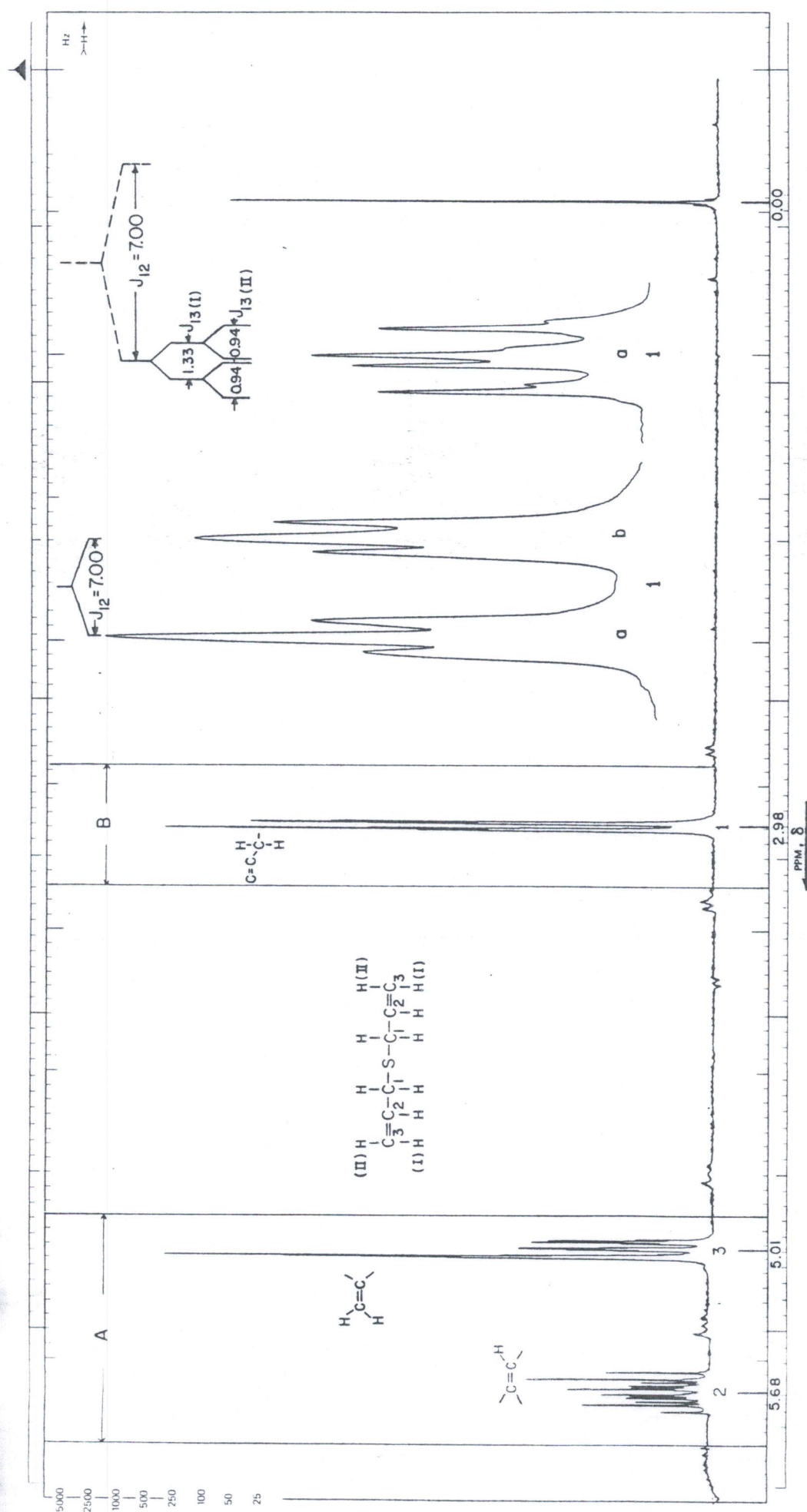
(b) - as determined by the author in 220 MHz
NMR spectrometer.

Figure 14: 220 MHz NMR spectrum of diallyl sulfide (in CS_2 using TMS as the internal standard) showing the olefinic (A) and allylic (B) protons. The doublet of the allylic protons at 2.98 δ (1) is also shown in an enlarged form and one of its signals (1a) is shown in better resolution as the doublet of a doublet, split by I and II(56).

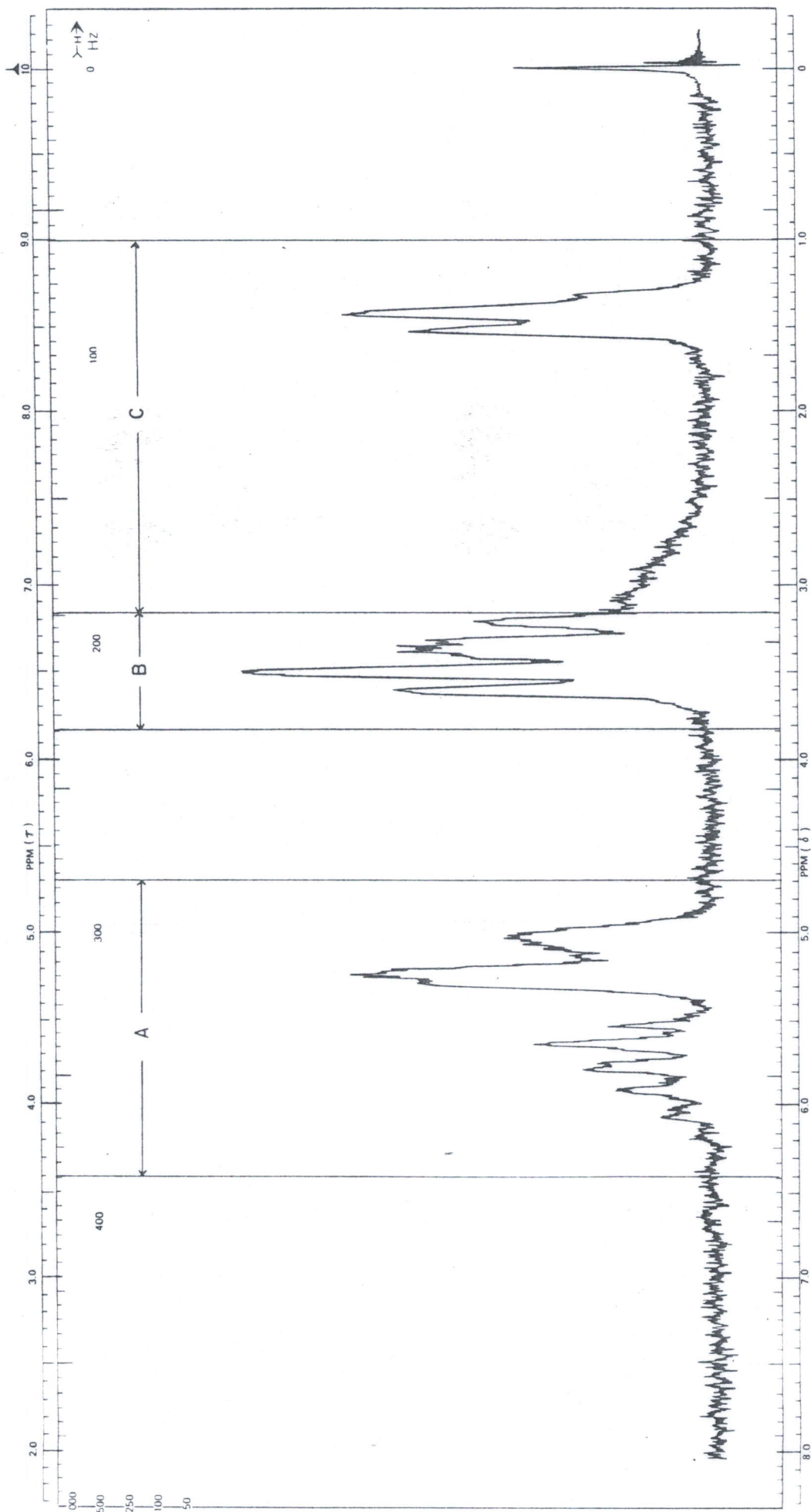62.

Figure 15: 60 MHz NMR spectrum of oligomeric alkenyl polysulfide of molecular weight 280, OAPS-280, (in CS$_2$ using TMS as the internal standard) showing the olefinic (A), allylic (B) and saturated (C) protons.
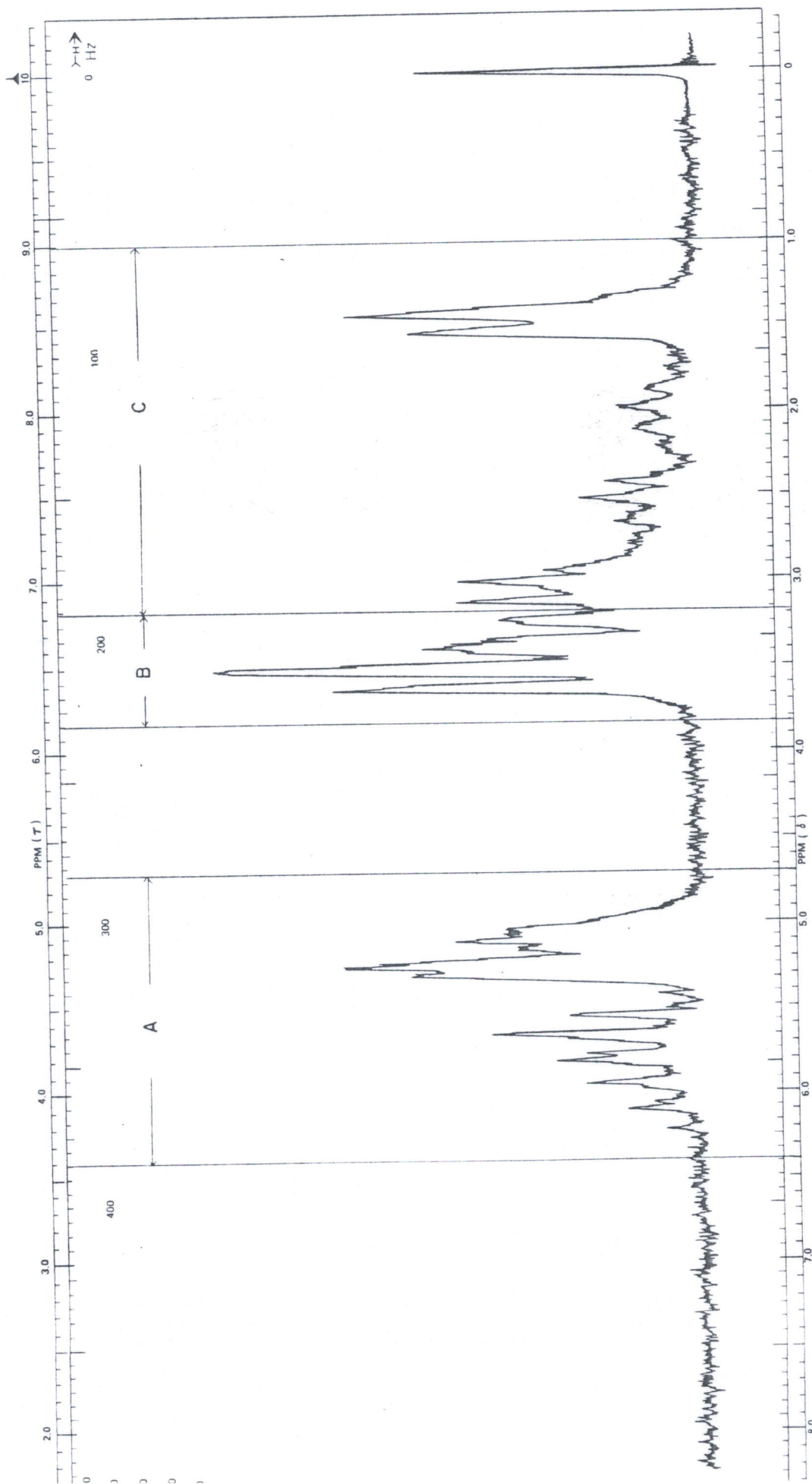
63.

Figure 16: 60 MHz NMR spectrum of oligomeric alkenyl polysulfide of molecular weight 350, OAPS-350, (in CS$_2$ using TMS as the internal standard) showing the olefinic (A), allylic (B) and saturated (C) protons.
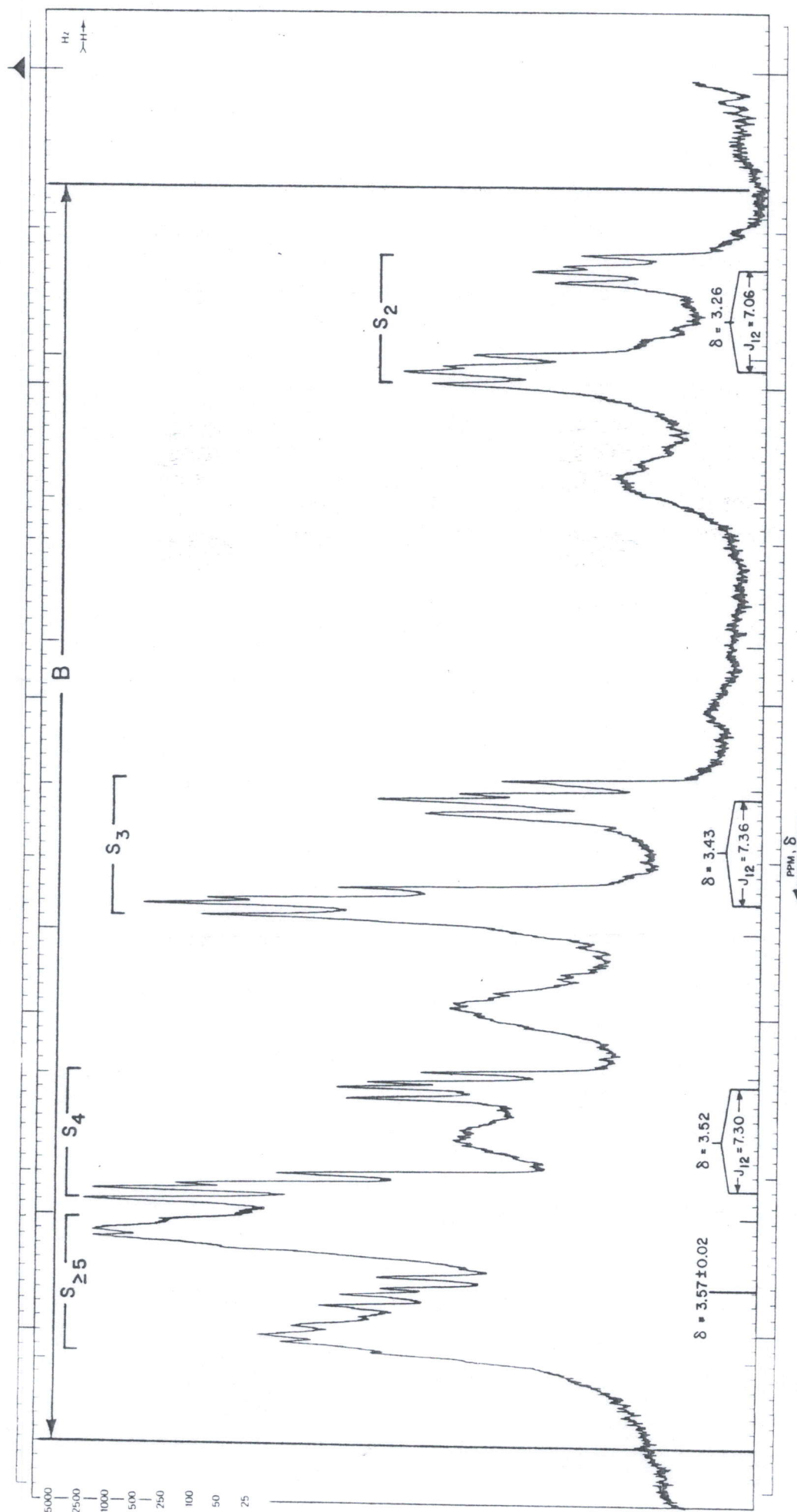
64.

Figure 17: 220 MHz NMR spectrum of the allylic protons (B) in oligomeric alkenyl polysulfide of molecular weight 350, OAPS-350, (in CS_2 using TMS as the internal standard). The doublet of a doublet signals for the allylic protons of the polysulfide distribution with sulfur ranks, 2, 3, 4 and ≥ 5 have been assigned as shown.

compounds, ethyl polysulfide and allyl polysulfide, both
having varying sulfur ranks, are shown in Table 10[54].
Similar behavior with some other polysulfides, RS_xR, and
polysulfanes, RS_xH, have also been reported[55]. Thus it
appears that it would be difficult by NMR analysis to
distinguish between high sulfur ranks, where x is greater
than 4. A 220 MHz NMR spectrum (in CS_2) of OAPS-350 in the
region B, the allylic protons, is shown in Figure 17. The
distinct chemical shifts, splitting pattern and coupling
constant (J_{12} on an average being 7.18 cps) help to unambigu-
ously assign the presence of x equal to 2, 3 and 4 as shown
(Figure 17). The signals around 3.57 ± 0.02 δ are attributed
to x ≥ 5. Since the saturated protons with x = 4 have about
the same chemical shift as the allylic protons with x = 1
(Table 10), the presence of monosulfide cannot be unambiguously
established. However, its concentration is expected to be
negligibly small[48]. The presence of some additional broad
lines seen in the spectrum (Figure 17) cannot be accounted for
at this time. Since the polysulfides of different sulfur ranks
have been assigned as shown, their approximate molar composi-
tions in OAPS-350 can be determined from the integration lines
(not shown) in Figure 17, and are shown below:

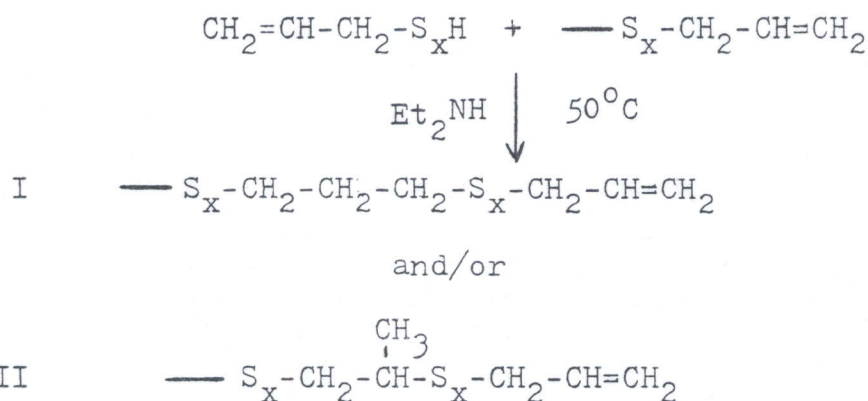| Sulfur rank, x	Molar composition of x
2 : 3 : 4 : ≥ 5 =	1.2 : 2.4 : 2.5 : 2.4

Assuming that the amounts of monosulfide and polysulfides of
sulfur rank greater than 5 are negligibly small, the number

average sulfur rank in OAPS-350 can be calculated as:

$$\bar{x} = \frac{1.3 \times 2 + 2.4 \times 3 + 2.5 \times 4 + 2.4 \times 5}{1.3 + 2.4 + 2.5 + 2.4} = 3.7$$

This calculated value of 3.7 is close to an observed value of 3.5, determined from elemental analysis and molecular weight.

Formation of polysulfane, $R-S_xH$, as an intermediate in sulfur-thiol reactions has been reported[11,49,50]. In the allyl thiol-sulfur reaction, sulfane/polysulfane can add to the allylic double bond in two ways, I and II, as shown below:

$$CH_2=CH-CH_2-S_xH \quad + \quad -S_x-CH_2-CH=CH_2$$

$$Et_2NH \downarrow 50^\circ C$$

I $\qquad -S_x-CH_2-CH_2-CH_2-S_x-CH_2-CH=CH_2$

and/or

$$\overset{\displaystyle CH_3}{\underset{\displaystyle}{}}$$

II $\qquad -S_x-CH_2-CH-S_x-CH_2-CH=CH_2$

Steric considerations give preference to the linear isomer, I, but electronic considerations for nucleophillic addition give preference to the branched isomer, II. Also, considering the mild reaction condition, a free-radical mechanism cannot be ruled out. The relatively high intensity of the signal around 1.45 δ in region C (Figures 15 and 16) gives evidence that the branched structure of the saturated protons is definitely present in large abundance and the linear structure may be present in small amounts.

A sample of OAPS of number average molecular weight 300 has been made by mixing appropriate amounts of

OAPS-280 (13.60 g), OAPS-295 (18.34 g) and OAPS-350 (9.10 g) as shown below:

$$\overline{M}_n \text{ of OAPS-300} = \frac{13.60 + 18.34 + 9.10}{\frac{13.60}{280} + \frac{18.34}{295} + \frac{9.10}{350}} = 300.1$$

The number of moles of double bonds per mole of OAPS-300 has been determined by NMR analysis taking benzene as the internal standard and integrating the spectrum (not shown) over the olefinic protons of benzene (7.2 δ) and OAPS-300. The number of olefinic protons in OAPS-300 can be calculated using the following expression:

$$\frac{\text{No.of olefinic protons in OAPS-300}}{\text{No.of aromatic protons in benzene}} = \frac{\frac{\text{Integral Height (OAPS-300)}}{\text{No.of moles of OAPS-300 per unit vol.}}}{\frac{\text{Integral Height (Benzene)}}{\text{No.of moles of benzene per unit vol.}}}$$

and it is found to be 5.3. This determined value of 1.8 (i.e., 5.3/3) for the number of moles of double bonds in OAPS-300 is close to the theoretical value of 2.0 within the experimental error involved in 60 MHz NMR analysis.
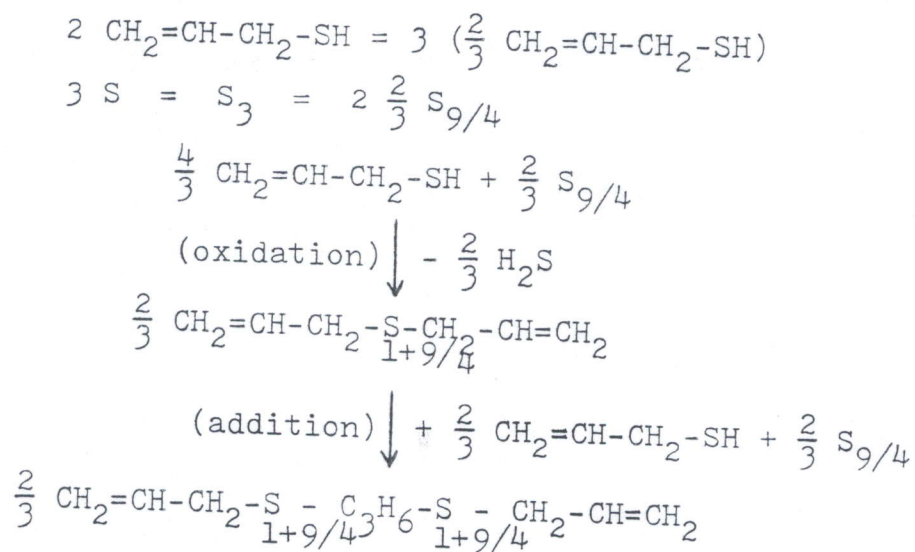
4.2.1.2. Theoretical Prediction of the Average Sulfur Rank in Oligomeric Alkenyl Polysulfide (OAPS):

It is expected and, in fact, observed with the samples of OAPS-280 ($\overline{x}$ = 4.0 and n = 0.4) and OAPS-350 ($\overline{x}$ = 3.5 and n = 1.0) that as the average degree of oligomerization, n, increases, the average sulfur rank, $\overline{x}$, decreases. In a general case, it can be shown for the reaction of A moles of allyl thiol with B g-atoms of sulfur that the value of $\overline{x}$ is given by:
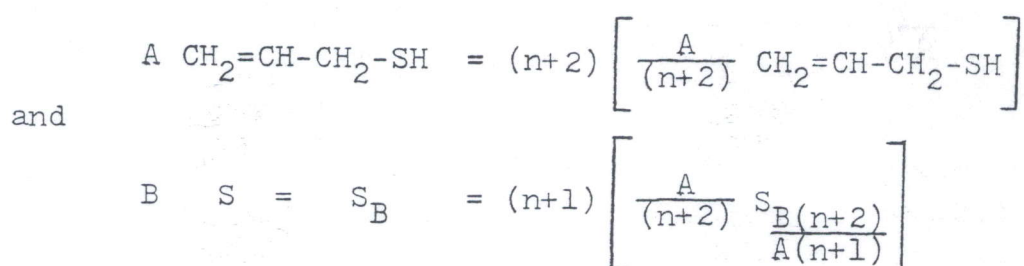
$$\bar{x} = 1 + \frac{B(n + 2)}{A(n + 1)}$$

In the reaction of 2 moles of dodecyl thiol with 3 g-atoms of sulfur, where n is always equal to zero, $\bar{x}$ is calculated to be 4 and also observed to be 4. In the reaction of 2 moles of allyl thiol with 3 g-atoms of sulfur, $\bar{x}$ is calculated to be 3.57 for $n = 0.4$ and 3.25 for $n = 1.0$. The respective observed sulfur ranks of 4.0 for $n = 0.4$ and 3.5 for $n = 1.0$ can be considered to be in agreement with the results predicted by the above equation. For this particular system, the equation shows that $\bar{x}$ will asymptotically approach a value of 2.5 if a high molecular weight polymer is formed.

An ideal reaction scheme for a system of 2 moles of allyl thiol with 3 g-atoms of sulfur is shown below to calculate x for n being strictly equal to 1:

$$2\ CH_2=CH-CH_2-SH = 3\ \left(\tfrac{2}{3}\ CH_2=CH-CH_2-SH\right)$$

$$3\ S\ =\ S_3\ =\ 2\tfrac{2}{3}\ S_{9/4}$$

$$\tfrac{4}{3}\ CH_2=CH-CH_2-SH + \tfrac{2}{3}\ S_{9/4}$$

$$\text{(oxidation)} \downarrow\ -\tfrac{2}{3}\ H_2S$$

$$\tfrac{2}{3}\ CH_2=CH-CH_2-S-CH_2-CH=CH_2$$
$${}_{1+9/4}$$

$$\text{(addition)} \downarrow\ +\tfrac{2}{3}\ CH_2=CH-CH_2-SH + \tfrac{2}{3}\ S_{9/4}$$

$$\tfrac{2}{3}\ CH_2=CH-CH_2-S - C_3H_6-S - CH_2-CH=CH_2$$
$${}_{1+9/4}{}_{1+9/4}$$

Considering this ideal reaction scheme for the general case of A moles of allyl thiol and B g-atoms of sulfur forming OAPS having the degree of oligomerization n and sulfur rank x, it can be shown that:

$$A \ CH_2=CH-CH_2-SH \ = \ (n+2) \left[\frac{A}{(n+2)} \ CH_2=CH-CH_2-SH \right]$$

and

$$B \ S \ = \ S_B \ = \ (n+1) \left[\frac{A}{(n+2)} \ S_{\frac{B(n+2)}{A(n+1)}} \right]$$

therefore,

$$x \ = \ 1 + \frac{B(n+2)}{A(n+1)}$$

It is expected that even if a distribution of oligomers of varying sulfur ranks is formed, the average value of x should remain constant and as predicted by the above equation provided the average value of n remains constant.

4.2.2. Copolymerization of Liquid Sulfur with Oligomeric Alkenyl Polysulfide (OAPS) Forming Crosslinked Polysulfide Polymers:

The "low temperature reaction (at $140^{\circ}C$)" of liquid sulfur with oligomeric alkenyl polysulfide (OAPS) has been investigated in the present study. OAPS has been found to readily dissolve in liquid sulfur at $140^{\circ}C$ and the melt viscosity of the solution increases with time due to a copolymerization reaction giving a dark brown product. The analytical characterization of the product is shown in Table 11. It is observed that the nature of the system with an equimolar composition of S_8 and OAPS is a viscous liquid

<div align="center">

Table 11.

Characterization of the Sulfur-Oligomeric Alkenyl Polysulfide
of Molecular Weight 350 (S_8:OAPS-350 = 1:1 molar) Reaction
Products Prepared at 140°C with Varying Reaction Times

</div>

Analytical Characterization	Reaction Time at 140°C			
	2 hrs.	4 hrs.	6 hrs.	8 hrs.
Nature of the product	viscous liquid	soft rubber	soft rubber	soft rubber
Unreacted free S_8, %	2.8	18.7	7.4	4.3
CS_2-soluble content, %	97.2	70.9	10.1	14.3
CS_2-insoluble content, %	0	10.4	82.5	81.4
$\overline{M}_n$ of CS_2-soluble polysulfide polymer	1155	1102	1504	1005
T_g onset temperature, °C (DTA, 15°C/min.)	-42±4	-26±6	-26±4	-26[a]

(a). T_g varied from -13 to -29°C; -26°C is the value
of the re-run of the previous -29°C sample,
heated to 31°C.

at a reaction time of 2 hours and a soft rubber at 4 hours and
longer. The conversion increases with time and therefore the
content of unreacted free S_8 decreases with time, with the
exception of the 2 hr. reaction product, the conversion at
the 8th hour being 95.7% $\left[\text{or } 4.3\%-S_8 \right]$. The content of CS_2-
soluble polysulfide polymer decreases with time, consequently
the content of crosslinked polysulfide polymer (CS_2-insoluble)
increases with time and finally levels off at about 80%. The
number average molecular weight, $\overline{M}_n$, (as determined by vapor
pressure osmometry using CS_2 as the solvent) of the CS_2-
soluble polymeric polysulfide has been determined to be about
1000-1500. It appears that when $\overline{M}_n$ exceeds this value, the
polymeric polysulfide is no longer soluble in CS_2. This
CS_2-insoluble product can be described as the crosslinked
polysulfide polymer, which, as expected, comprises the major
part of the product at high conversion. It is observed that
the "T_g-onset temperature" (which is a little lower than the
"T_g-extrapolated onset temperature" that will later be
accepted as "correct T_g") of the soft rubber is -26°C. Once
again, the 2 hr. product (viscous liquid) is an exception
with a T_g of -42°C. The initial low free S_8 content and
liquid nature of the product (i.e., the 2 hr. product)
suggests that insertion of sulfur into polysulfide linkages
is an important reaction in the early stages, though it cannot
be explained in detail at the present time. Subsequent
conversion and cross-linking are more or less consistent with

what is expected from a crosslinking polymerization reaction.

The IR spectra of OAPS-350 and the copolymer made from an equimolar composition of S_8 and OAPS-350 by reacting 8 hours at $140^\circ C$ are shown in Figures 18 and 19 respectively. The stretching band at 1630 cm^{-1} for the double bond in OAPS-350 (Figure 18) is observed to completely disappear in the copolymer (Figure 19). Since the reaction conversion for this system is more than 95% as determined by free sulfur analysis mentioned earlier, the ideal structure of the network polysulfide polymer can be represented as shown below assuming a 100% conversion:

$$
\begin{array}{c}
\text{---}\ CH_2\text{-----}CH\text{-----}S_{x_2}\text{---} \\
| \\
CH_2 \\
| \\
S_{x_1} \\
\overline{C_3H_6} \\
| \\
S_{x_1}\ \Big]_n \\
| \\
CH_2 \\
| \\
\text{---}S_{x_2}\text{-----}CH\text{-----}CH_2\text{---}
\end{array}
$$
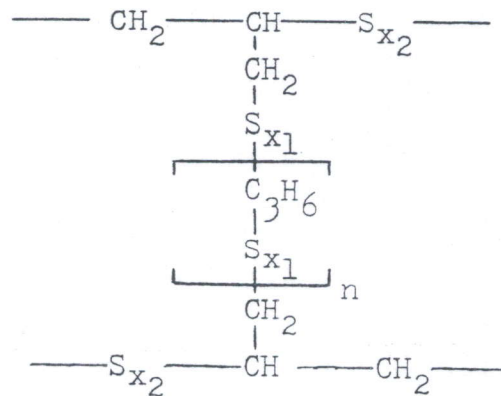
The average values of the different parameters above are: $n = 1.0$, $x_1 = 3.5$ and $x_2 = 4.0$. However, the sulfur ranks x_1 and x_2 may not be distinguishable and may have an average value of $\frac{1}{2}(x_1 + x_2)$ equal to 3.75 for OAPS-350 where $n = 1.0$, because the sulfur ranks of "Thiokol" polymers when heated with sulfur are known to increase[11].

The presence of the allylic protons in OAPS may give rise to polysulfide structures substituted at the allylic
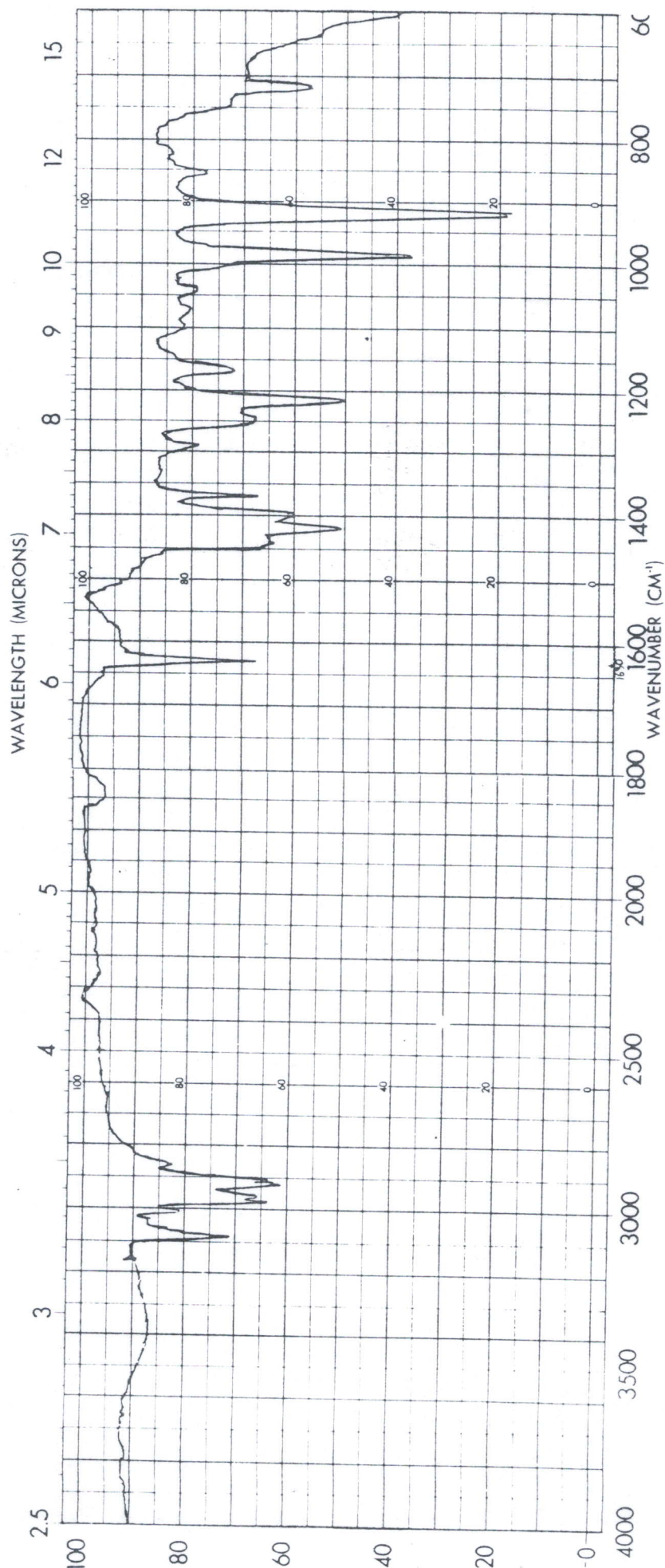
Figure 18: IR spectrum of oligomeric alkenyl polusulfide of molecular weight 350 (OAPS-350), the sample is a liquid film in between two sodium chloride plates.
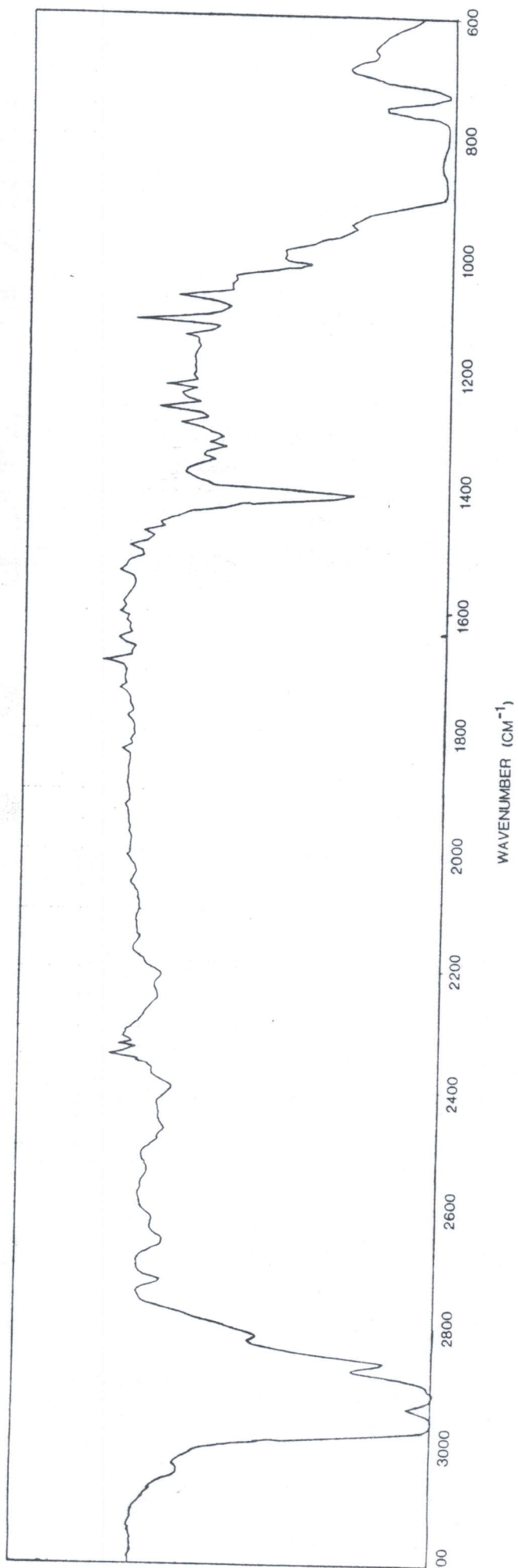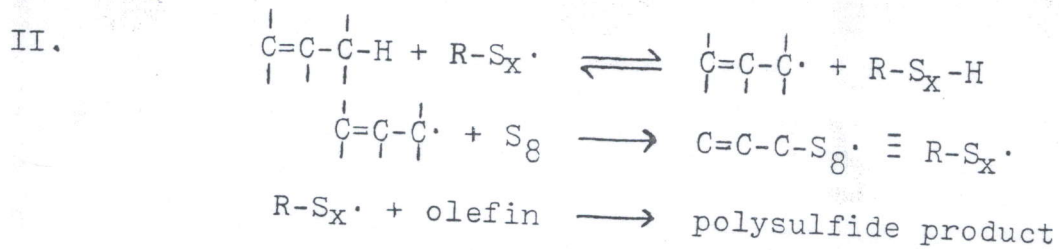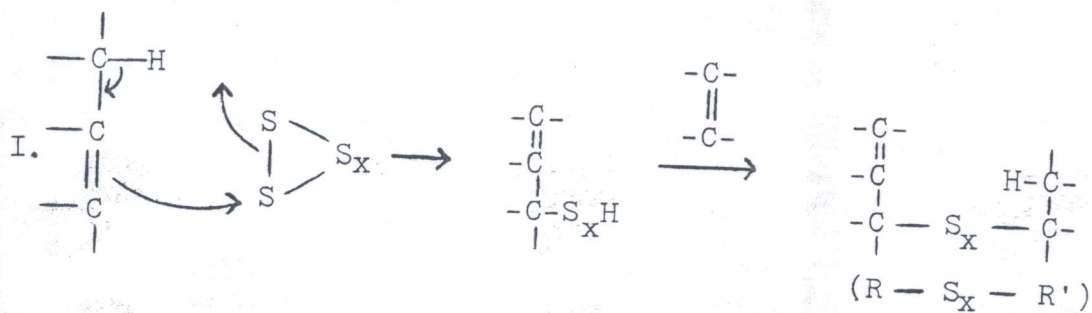
74.

Figure 19: FT-IR spectrum of a film sample of crosslinked polymeric polysulfide obtained from the 8 hr equimolar sulfur (S_8) - oligomeric alkenyl polysulfide of molecular weight 350 (OAPS-350) reaction at 140°C.

75.

carbon.   Possible mechanisms for this are shown below[58].

I.

II.

$$C=C-C-H + R-S_x\cdot \rightleftharpoons C=C-C\cdot + R-S_x-H$$

$$C=C-C\cdot + S_8 \longrightarrow C=C-C-S_8\cdot \equiv R-S_x\cdot$$

$$R-S_x\cdot + olefin \longrightarrow polysulfide\ product$$

Such structures give rise to residual double bonds which, if they are not further sulfurated, may remain in the product. Since the IR spectrum (Figure 19) does not show any olefinic stretching band near 1600 cm^{-1}, it appears that allylic substitution products are negligibly small, if at all present.

4.3 Structure-Property Studies on the Copolymers and Terpolymers of Sulfur, Oligomeric Alkenyl Poly-Sulfide (OAPS) and Dicyclopentadiene (DCP)/exo-Cyclic Trithia Derivative of Dicyclopentadiene (DCP-S_3):

Structure-property studies have been carried out on the sulfur:DCP, sulfur:DCP-S_3 and sulfur:OAPS copolymer systems and on the sulfur:OAPS DCP-S_3 terpolymer system. The properties of interest considered in the investigation of these new polymeric materials are the stability of the materials against sulfur crystallization, their glass transition temperatures, mechanical properties and chemical stress relaxation, which is a property characteristic of polysulfide polymers.

4.3.1. Crystallization of Sulfur:

Plastic sulfur, which is a mixture of amorphous S_8 rings and amorphous polymeric sulfur, is thermodynamically unstable, and its instability has been discussed in detail earlier. It undergoes embrittlement at ambient temperature due to the rapid crystallization of octameric sulfur to orthorhombic sulfur. Elemental sulfur has been proposed for a range of applications[11], but the development of many of these applications has been reported to be hindered by the propensity of sulfur to revert rapidly to the crystalline S_α form[11]. Therefore, it is important to investigate and develop copolymeric materials of sulfur which will be stable against crystallization of sulfur under ambient conditions.

Quantitative determination of the allotropes of sulfur has been carried out by Blight, et al. on dicyclopentadiene