Thermal interaction of liquid sulfur with several olefinic systems at 140-170°C forming polymeric polusulfides has been reported[11]. Molecular weights of the soluble polymeric polysulfide formed with the olefinic systems investigated are rather low, about 3000-7000, and the polysulfides appear to have widely varying sulfur ranks. Anionic copolymerization of elemental sulfur with 1,2-propylene sulfide at temperatures above 60°C has been reported to give high molecular weight polymers ($\overline{M}_n = 10^4$ to 10^5) with the sulfur rank $9 > x > 1$[29]. The above reactions and the polycondensation of α, ω-dihaloalkanes with alkali metal polysulfides formed by the reaction of sulfide anion with sulfur, always give a distribution of sulfur ranks in the polymeric polysulfides. Polymeric polysulfides of homogeneous and uniform sulfur ranks, (e.g., sulfur ranks of 3 and 4) have been synthesized by the reaction of α, ω-dithiols and with dichloromonosulfane and dichlorodisulfane, respectively[30]. The molecular weights here are low ($\overline{M}_n = 10^3$)[30].
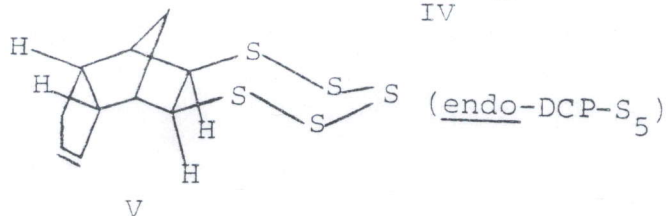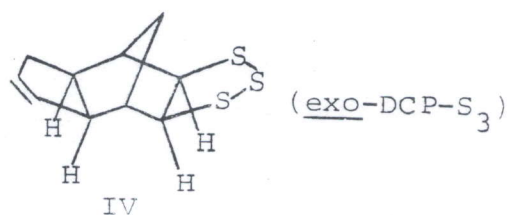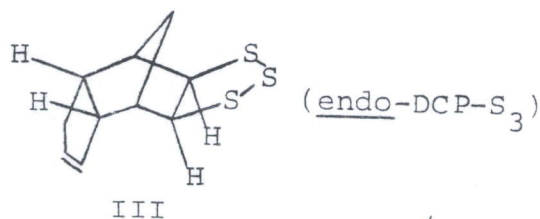
A systematic approach to the characterization and structure-property studies on the polymeric polysulfides formed by the interaction of liquid sulfur with certain olefinic systems at 140°C has been investigated here. The olefinic systems of interest are dicyclopentadiene (DCP) and an oligomeric alkenyl polysulfide (OAPS). DCP is a rigid and bulky olefin which gives linear polymer after a relatively short reaction time, and crosslinked polymer after longer times. OAPS is a linear and flexible olefin, which is readily

soluble in liquid sulfur. It copolymerizes with sulfur to give crosslinked polymeric polysulfides.

4.1. <u>Synthesis and Characterization of the Sulfur-Dicyclo-
pentadiene (DCP) Copolymeric System</u>:

(DCP)

(DCP-S$_{3 \text{ or } 5}$)
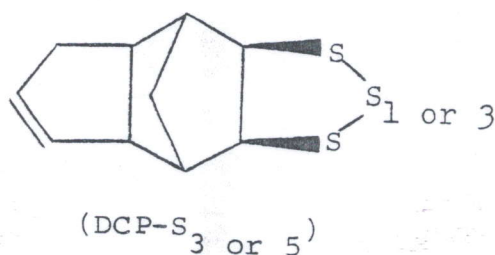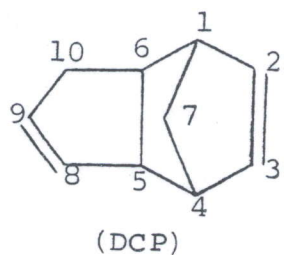
Dicyclopentadiene has been reported to react with
sulfur to give, initially, low molecular-weight polysulfides
(<u>e</u>.<u>g</u>., tri- and pentasulfides). As reaction proceeds at 140°C
they convert to higher molecular weight polymers[31]. In
contrast, styrene has been reported, to give initially high
molecular weight polymers which depolymerize as the reaction
proceeds to give 2,4-diphenylthiophene[31]. The low molecular
weight polysulfides formed with DCP, e.g., <u>exo</u>-cyclic trithia
derivative of DCP (<u>i</u>.<u>e</u>., <u>endo</u>-DCP), appear to be "inter-
mediates" in the sulfur-DCP copolymerization[31].

(<u>endo</u>-DCP)

I

(<u>exo</u>-DCP)

II

(<u>endo</u>-DCP-S$_3$)

III

(<u>exo</u>-DCP-S$_3$)

IV

(<u>endo</u>-DCP-S$_5$)

V
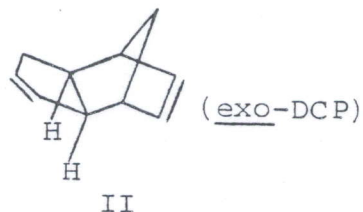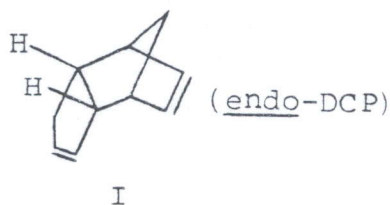
In the present study both the _endo_- and _exo_-isomer of dicyclopentadiene, I and II, respectively, have been synthesized for copolymerization with sulfur to elucidate the effect of steric constraints. Also, the _exo_-cyclic trithia derivatives of _endo_- and _exo_-dicyclopentadiene (_endo_-/_exo_-DCP-S_3), III and IV, respectively, have been synthesized for copolymerization studies with sulfur. The DCP-S_3 monomers dissolve very readily in liquid S_8, whereas the DCP monomers dissolve in liquid S_8 only with difficulty. Therefore, the DCP-S_3 monomers are preferred over the DCP monomers for synthesis of terpolymers with sulfur and OAPS for structure-property studies.

The behavior of melt viscosity and surface tension of sulfur-DCP solutions are of practical importance because they are used as sprayable coatings. Also these studies are expected to give some understanding about the polymerization reaction as will be described later and, therefore, have been included in the present study.

4.1.1. <u>Synthesis of the Stereoisomers of DCP and the "Intermediates", the _exo_-Cyclic Trithia Derivatives of Dicyclopentadiene (DCP-S_3):</u>

Commercially available DCP is almost exclusively the _endo_-isomer, I, formed from cyclopentadiene by dimerization according to the _cis_ addition rule of Alder[32]. However, the _exo_-isomer, II, is the thermodynamically more stable isomer[32]. _endo_-DCP has been purified by distillation of commercial DCP under reduced pressure[33]. _exo_-DCP has been synthesized by the following reaction scheme[24,25,33]:
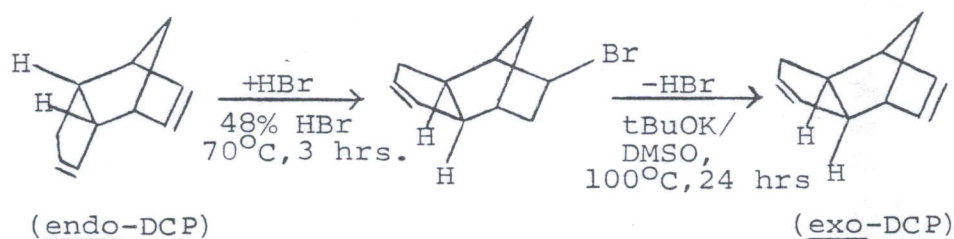
(endo-DCP)   (exo-DCP)

The intermediate above, exo-bromo-dihydro-exo-DCP, is formed
by the Meerwein-Wagner rearrangement[25,34]. The NMR spectra
(in CS_2) of endo-DCP and exo-DCP are shown in Figures 2 and 3
respectively. In the range of about 5-6 δ where olefinic
protons usually appear, it is observed that the norbornenyl
unsaturations in endo- and exo-DCP are more downfield than
the respective cyclopentenyl unsaturations, and the cyclo-
pentenyl unsaturation in endo-DCP gives a singlet and in
exo-DCP a multiplet, thus rendering it possible to distinguish
easily between the two isomers[35].

III and IV have been synthesized from I and II,
respectively, by the active sulfuration method of Shields,
et al.[26]. NMR spectra (in CS_2) of III and IV are shown in
Figures 4 and 5, respectively. It is observed that the
norbornenyl unsaturations disappear, the cyclopentenyl
unsaturation of the isomers remain and a doublet appears at
3.59 δ (Figure 4) and 3.62 δ (Figure 5) for the endo- and
exo-isomer, respectively. This doublet is attributed to the
pair of cis-endo protons in the trithiapentacyclic ring of
$DCP-S_3$[26].

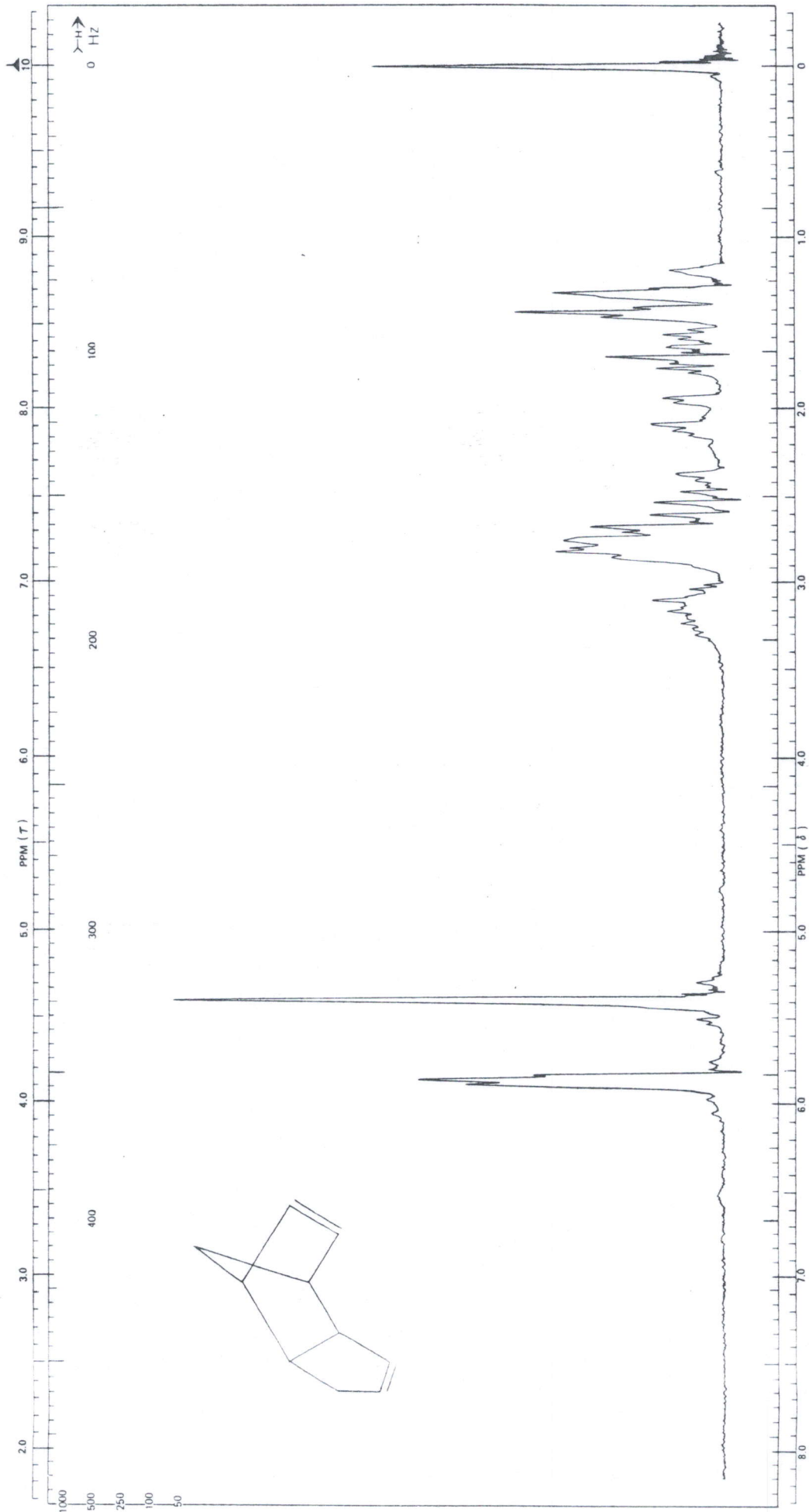Figure 2: 60 MHz NMR spectrum of <u>endo</u>-dicyclopentadiene (<u>endo</u>-DCP) in CS_2 using TMS as the internal standard.

29.

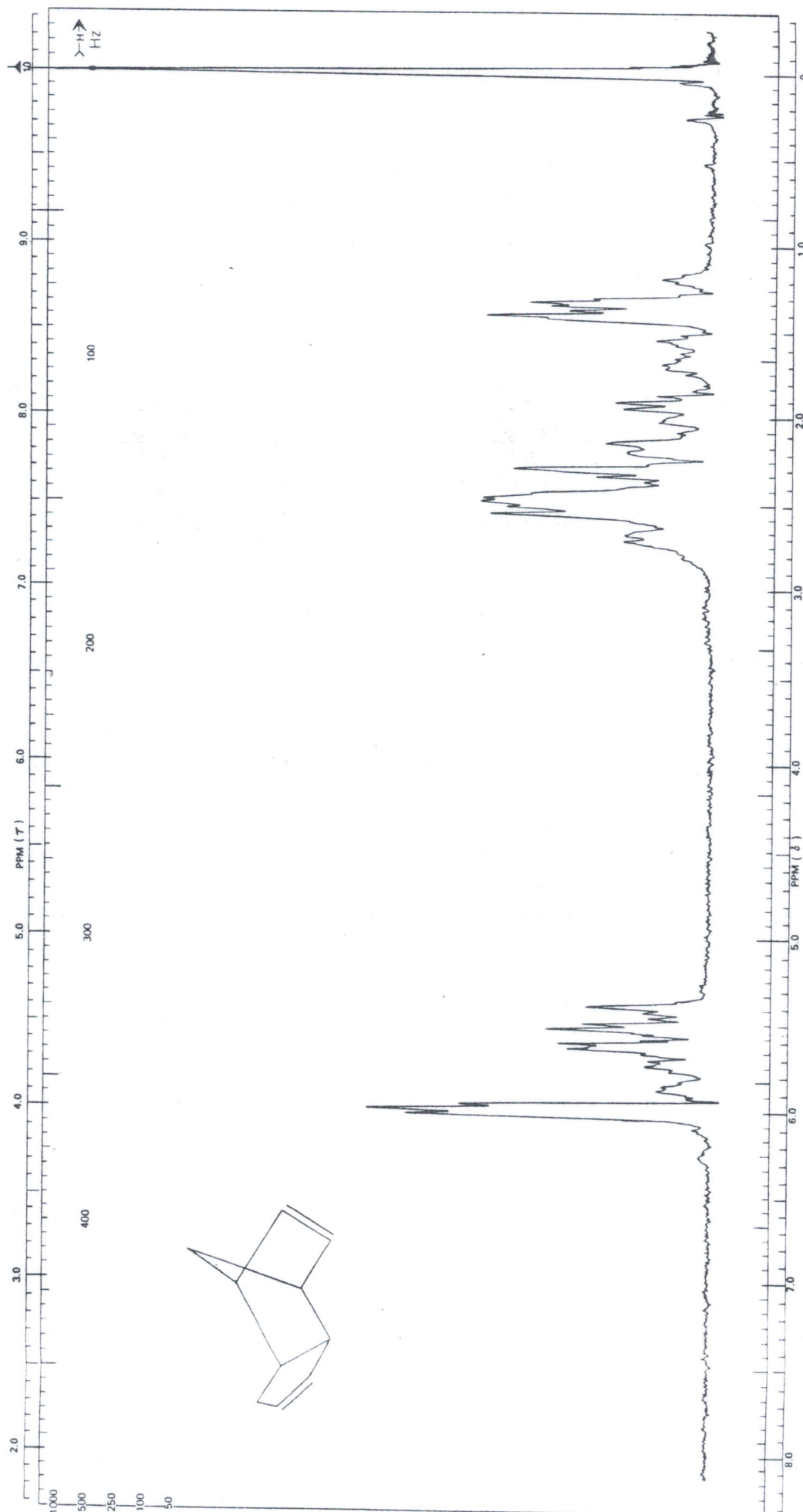Figure 3: 60 MHz NMR spectrum of exo-dicyclopentadiene (exo-DCP) in CS$_2$ using TMS as the internal standard.
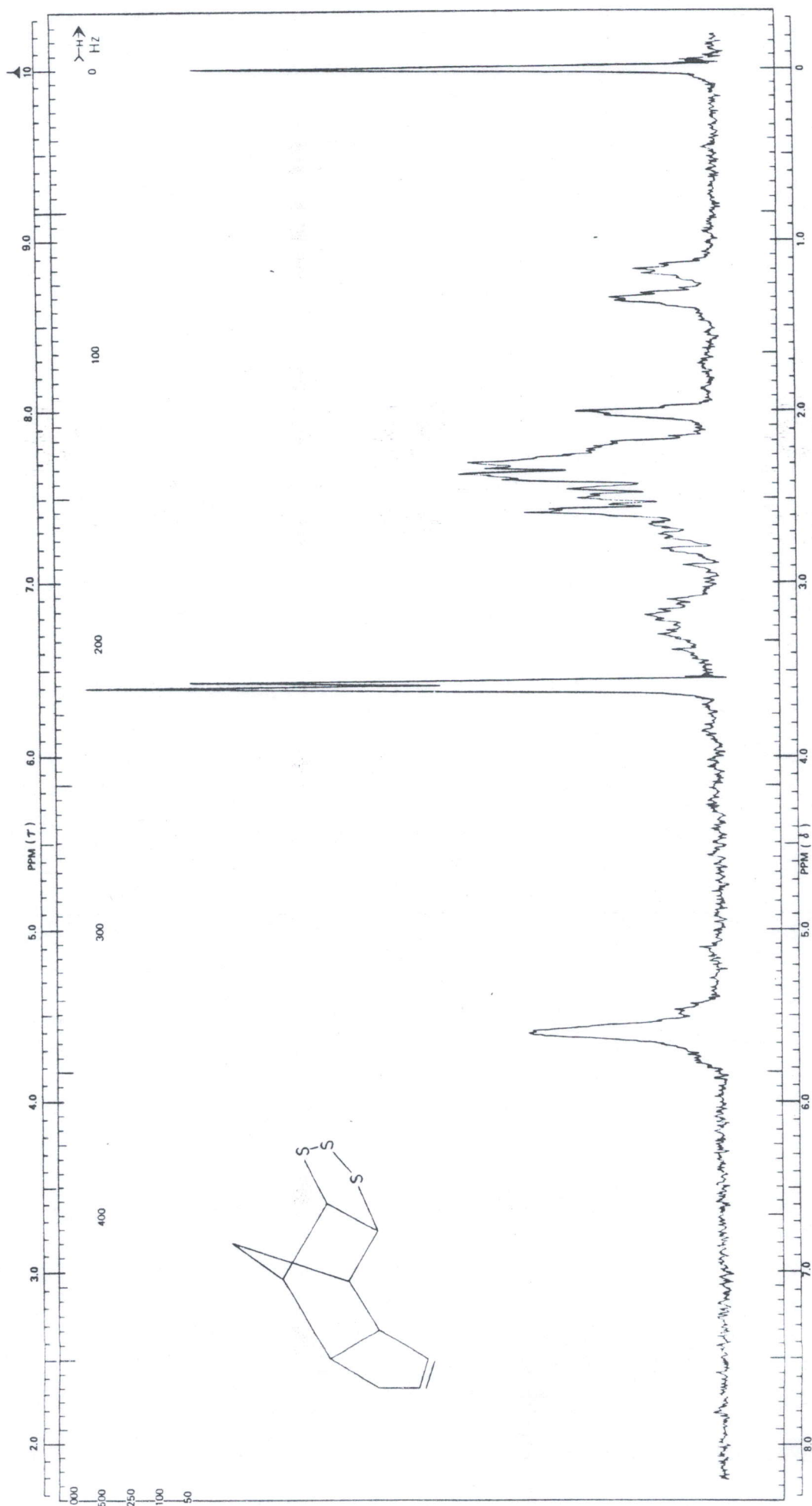
30.

Figure 4: 60 MHz NMR spectrum of exo-cyclic trithia derivative of endo-dicyclopentadiene (endo-DCP-S_3) in CS_2 using TMS as the internal standard.
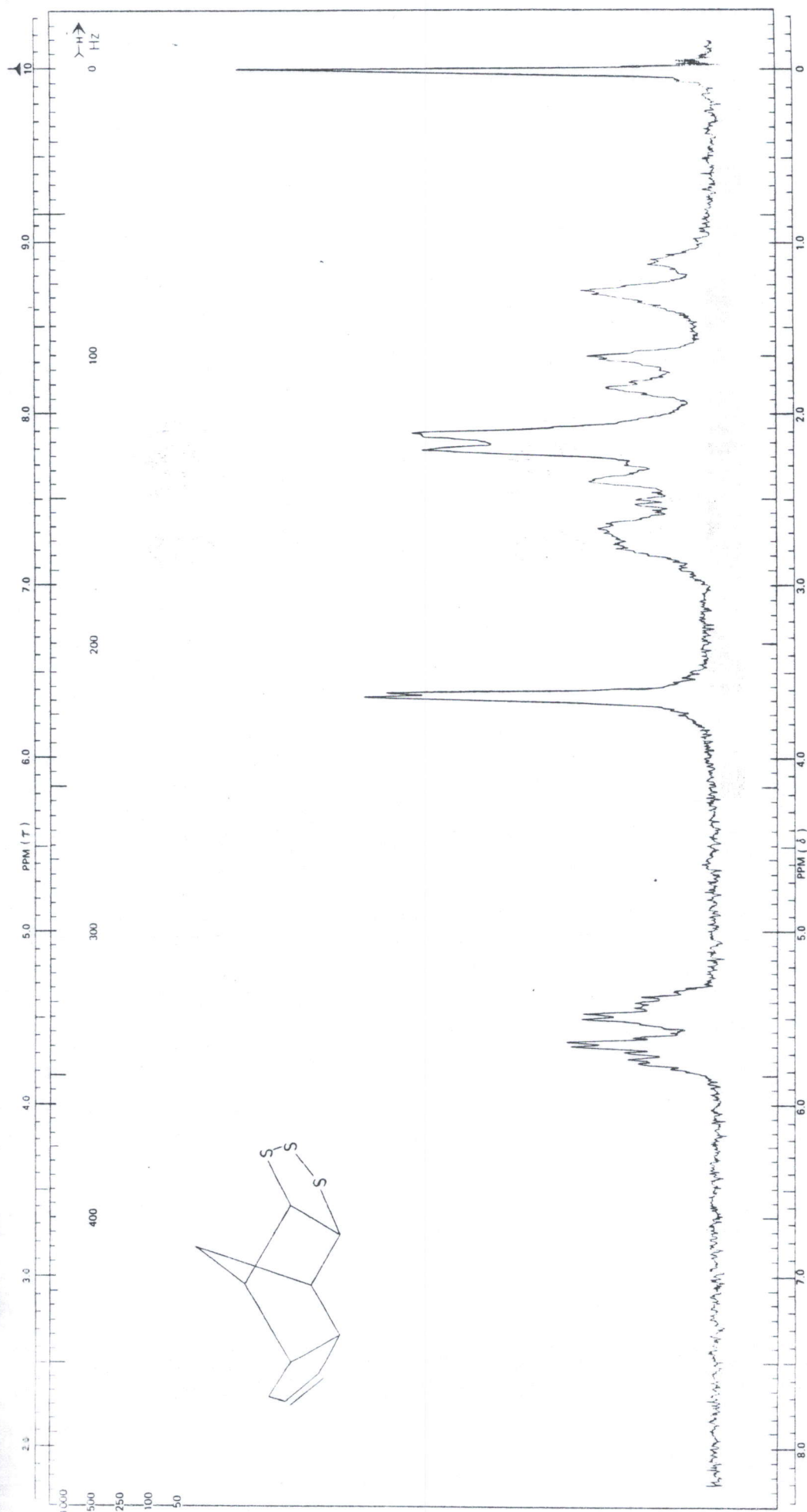
31.

Figure 5: 60 MHz NMR spectrum of exo-cyclic trithia derivative of exo-dicyclopentadiene (exo-DCP-S₃) in CS₂ using TMS as the internal standard.

32.

4.1.2. Copolymerization of Liquid Sulfur with Dicyclopentadiene (DCP) and exo-Cyclic Trithia Derivative of Dicyclopentadiene (DCP-S$_3$) Forming Linear and Crosslinked Polymeric Polysulfides:

Sulfur-olefin reactions are catagorized as low temperature (up to 140°C) and high temperature (higher than 140°C) reactions[36]. Though a free-radical chain growth mechanism was proposed initially for the low temperature reactions[36], a cationic chain growth mechanism proposed later appears to have more experimental support[36]. However, these were not polymer forming reaction conditions. High temperature reactions are complex and no unique mechanism has been proposed, although both free-radical and cationic mechanisms can probably occur. The liquid sulfur-olefin low temperature reactions have been investigated here.

It has been shown via copolymerization experiments that the norbornenyl unsaturation in endo-DCP is twice as reactive as the cyclopentenyl unsaturation; exo-DCP is twice as reactive as endo-DCP, and endo-DCP is 7.5 times more reactive than propylene[32]. DCP (boiling points for both the isomers are the same, which is 170°C) is soluble in liquid sulfur at 140°C in all proportions and the melt viscosity of the sulfur-DCP solution increases with time due to a copolymerization reaction. An exothermic sulfur-DCP reaction is clearly evident in the DSC thermograms (Figure 6) where the exotherm is observed to start at about 140°C with a feed of about 20 weight % DCP.

The sulfur-DCP (i.e., endo-DCP) reaction product initially containing 40% endo-DCP (W/W sulfur) is reported to
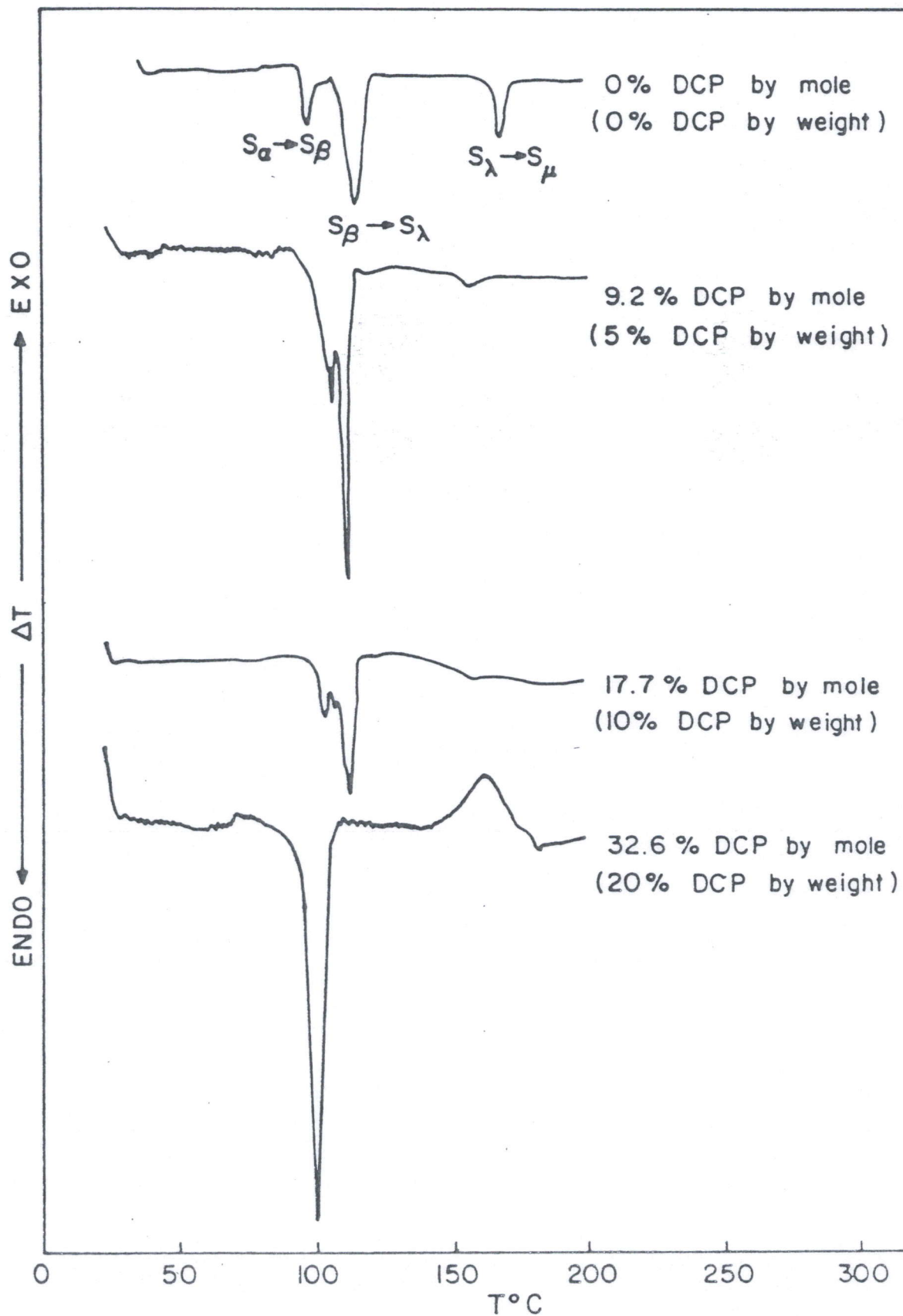
Figure 6: DSC thermograms of sulfur - <u>endo</u>-dicyclopentadiene (DCP) mixtures with varying compositions as shown. (Heating rate in DSC is $10^{\circ}C$ min^{-1}).

contain 64.3% polymeric polysulfide and 35.7% unreacted
free sulfur in the form of liquid-S_8 after 10 hrs. of
reaction at $140^\circ C$[31]. The polymeric polysulfide ($\overline{M}_n$ = 3390)
has been described by the average structure, VI, shown below[31].

$$\left[S_{6.75} \right]$$
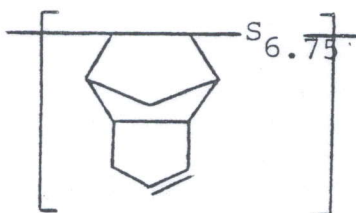
VI

The analytical characterization of the equimolar
S_8-DCP reaction product after 4 hours of reaction at $140^\circ C$
is summarized in Table 4 for both isomers. It is observed
that no crosslinked polymeric polysulfide (i.e., CS_2-insoluble
material) is formed. The crosslinking could possibly occur
by the reaction of residual cyclopentenyl unsaturation in DCP.
The polymeric polysulfide is formed by reaction of the
norbornenyl unsaturation in DCP. The conversion in the
S_8-exo-DCP system is observed to be higher than that of the
S_8-endo-DCP system and also the molecular weight ($\overline{M}_n$) of the
CS_2-soluble polymeric polysulfide of the former is about twice
that of the latter (Table 4). Such behavior is consistent
with the relative reactivities of the various unsaturations
mentioned earlier.

The analytical characterization of the sulfur-DCP-S_3
reaction product prepared with a feed composition of 5 g-atoms
of sulfur to 1 mole of DCP-S_3 and 4 hours of reaction at $140^\circ C$
is shown in Table 5 for both the isomers. It is observed

Table 4.

Characterization of the Sulfur-Dicyclopentadiene
(S_8:DCP = 1:1 molar) Reaction Product Prepared
from the 4 hr. Reaction at 140°C.

Analytical Characterization	endo-DCP	exo-DCP
Free S_8, %	21.8	12.6
CS_2-insoluble content, %	0	0
CS_2-soluble content, %	78.2	87.4
$\overline{M}_n$ of soluble polymeric Polysulfide	526	1047

Table 5.

Characterization of the Sulfur-exo-Cyclic Trithia
Derivative of Dicyclopentadiene (S : $DCP-S_3$ =
5 g-atoms:1 mole) Reaction Product Prepared from
the 4 hr. Reaction at 140°C.

Analytical Characterization	endo-$DCP-S_3$	exo-$DCP-S_3$
Free S_8, %	18.7	20.3
CS_2-insoluble content, %	12.1	10.2
CS_2-soluble content, %	69.2	69.5
$\overline{M}_n$ of soluble polymeric Polysulfide	683	774

that crosslinked polymeric polysulfides are formed with both
the isomers in this case. However, the conversion and the
molecular weight ($\overline{M}_n$) of the CS_2-soluble polymeric poly-
sulfides are about the same for both isomers, unlike the case
with DCP. Molecular weights of the linear polymeric poly-
sulfides (i.e., CS_2-soluble) in all the systems are observed
to be low, but the conversions are high (Tables 4 and 5).

The NMR spectra (in CS_2) of the polysulfide products
formed from the equimolar sulfur-DCP reactions for 3 hours at
140°C with the endo- and exo-isomers are shown in Figures 7
and 8, respectively. The norbornenyl unsaturations are
observed to undergo complete reaction. The singlet and
multiplet cyclopentenyl unsaturations of the respective olefins
are observed around 5.60 δ in Figures 7 and 8, respectively,
showing that there is no Meerwein-Wagner type rearrange-
ment[25,34]. There are two additional signals of interest
(Figures 7 and 8), one at 3.55 δ and the other at 3.85 δ.
The 2,3-cis-endo-protons in the exo-cyclic trithia and penta-
thia derivatives of endo-DCP, endo-DCP-S_3 (III) and endo-DCP-
S_5 (V), respectively, have been assigned chemical shifts
(in CCl_4, 100 MHz NMR) of 3.60 δ and 3.86 δ, respectively[31].
Therefore the signal at 3.85 δ (Figures 7 and 8) is attributed
to the formation of cis-exo-cyclic pentathia derivatives of
the respective isomers of DCP[31]. The signal at 3.55 δ
(Figures 7 and 8) is attributed to the formation of the exo-
cyclic trithia derivatives, III and IV, as well as polymeric

Figure 7: 60 MHz NMR spectrum (in CS_2 with TMS as the internal standard) of the sulfurated products of endo-dicyclopentadiene (endo-DCP), obtained from the 3 hr equimolar S_8-DCP reaction at 140°C.
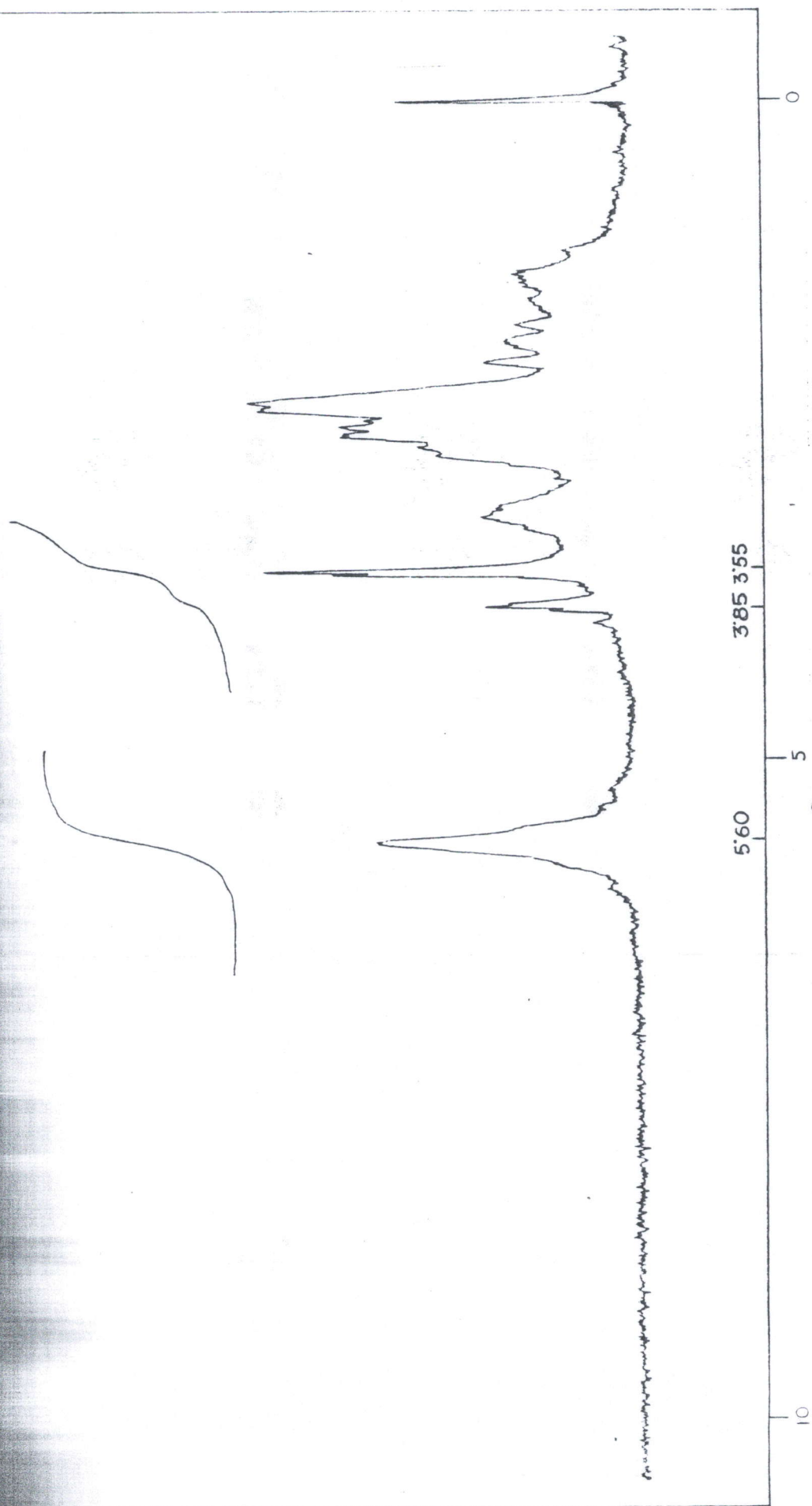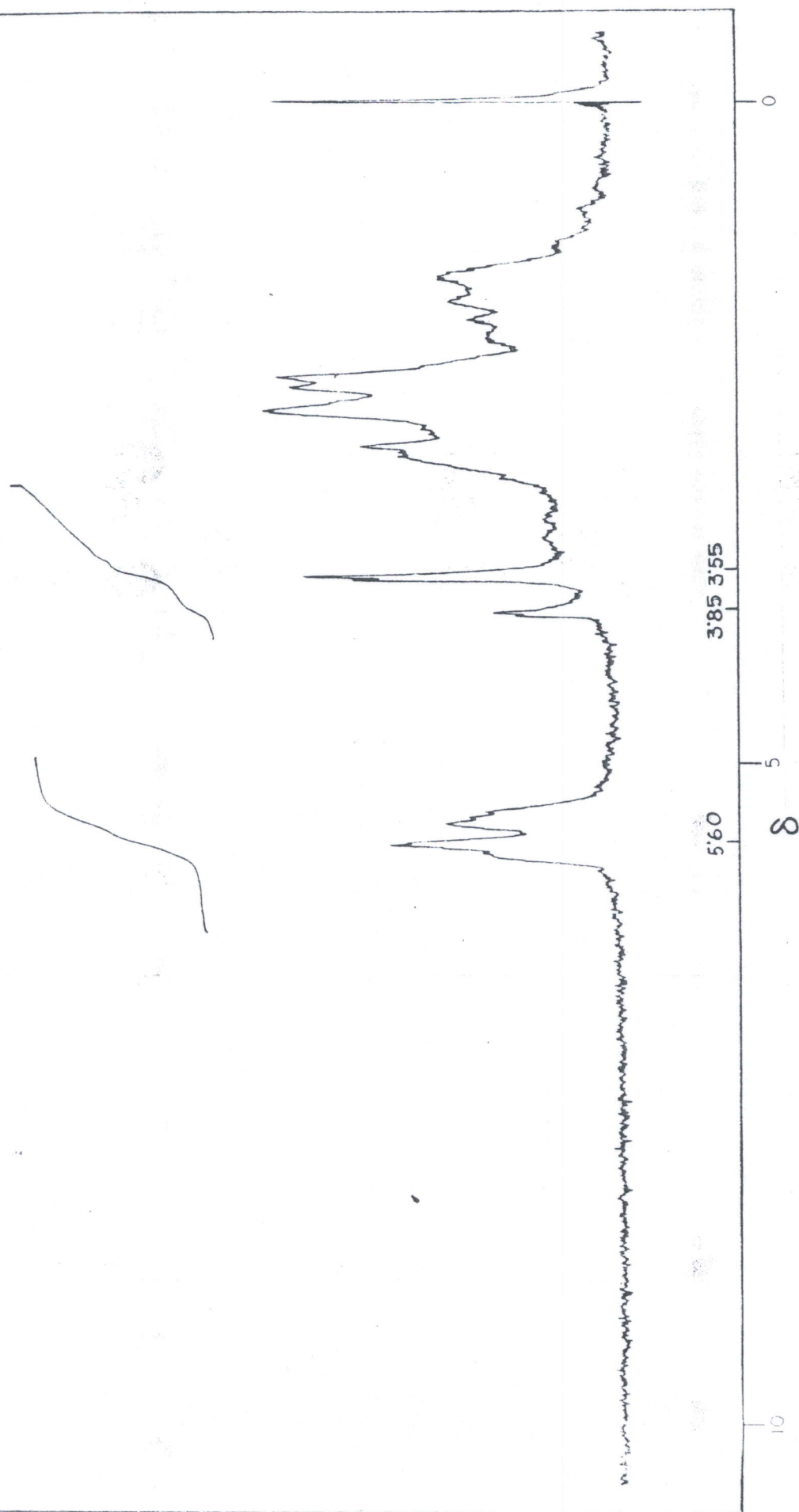
38.

Figure 8: 60 MHz NMR spectrum (in CS_2 with TMS as the internal standard) of the sulfurated products of exo-dicyclopentadiene (exo-DCP), obtained from the 3 hr equimolar S_8-DCP reaction at 140°C.

39.

polysulfides, VII and VIII, formed from the respective
olefins[31]. Hence, it appears that all the sulfurated
products formed through the norbornenyl unsaturations of
endo- and exo-DCP are cis-exo in nature. It has been

$$\text{VII} \qquad\qquad \text{VIII}$$
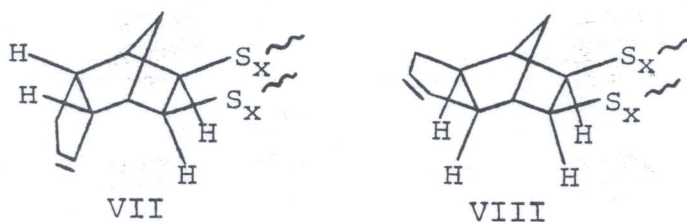
observed that the sulfurated products formed from the
sulfur-DCP-S_3 systems have the same characteristics in their
NMR spectra as those from the sulfur-DCP systems of the
respective isomers. Therefore, the same cis-exo-cyclic penta-
thia derivatives and cis-exo polymeric polysulfides, VII and
VIII, are formed from the sulfur-DCP-S_3 systems.

The fraction of CS_2-insoluble polymeric polysulfides
increases with increasing reaction time. This is clear from
the data in Table 6 which shows the composition of the sulfur-
endo-DCP (25% DCP, W/W sulfur) reaction products formed at
varying reaction times at $140^{\circ}C$[31]. This is attributed to
the formation of crosslinked polymeric polysulfides by
sulfuration of the residual cyclopentenyl unsaturation sites.
Thus, it is observed that the formation of crosslinked
polymeric polysulfides increases with reaction time. The
sulfur rank of the polymeric polysulfide is expected to depend
on feed composition and reaction conversion.

Table 6.

Composition of the Sulfur-endo-dicyclopentadiene
(25% DCP) Reaction Products with Respect to
Reaction Time at 140°C.

Reaction time (hr.)	Unreacted Sulfur (%)	Total Polymeric Polysulfide (%)	CS_2-insoluble Polymeric Polysulfide (%)
3	45.3	54.7	15.1
20	31.3	68.7	56.6

4.1.3.   Evidence for a Step-Growth Mechanism of Poly-merization in the Sulfur-Dicyclopentadiene (DCP) System.

The behavior of melt viscosity and surface tension of the sulfur-DCP (the endo isomer) solutions have been analyzed and appears to give evidence for a step-growth mechanism of polymerization. This is consistent with the results of Blight, et al. who have shown by analytical characterization that as the reaction time increases the molecular weight of the polymeric polysulfides formed in the sulfur-DCP system increases[31].

4.1.3.1.   Behavior of the Melt Viscosity of Sulfur-dicyclopentadiene (DCP) Solutions:

The melt viscosity of the sulfur-DCP solution increases with time due to a copolymerization reaction. Though the norbornenyl unsaturation in DCP is observed to disappear in the early stage of the reaction by NMR analysis, the viscosity has been found to increase even afterwards. This can be considered to be an indication for a step-growth mechanism of polymerization[37].

The melt viscosity behavior of the sulfur-DCP system has recently been reported, but only qualitatively and only over a narrow range of compositions[38]. The viscosity of sulfur measured by the capillary method by Bacon and Fanelli are considered to be the best[39,40,41]. Recently the viscosity of sulfur measured by an apparatus containing an electric motor and a rotating cylinder has been reported[42]. Viscosity of the sulfur-DCP solutions are measured in the present study with a Brookfield synchro-lectric viscometer.

The exponential behavior of viscosity as a function of time for varying compositions of S_8 and DCP is shown in Figures 9 and 10. The pronounced effect of temperature is seen by comparing Figures 9 and 11. The maximum rate for the logarithmic increase in viscosity is observed for an equimolar feed of S_8 and DCP in Figure 12. Such behavior appears to support a "step-growth copolymerization mechanism"[37]. It has been pointed out by Pryor in sulfur-olefin reactions that only carbon-sulfur bonds are formed and no new carbon-carbon bonds are formed[43]. Therefore, in such a copolymerization reaction, one expects to get a strictly alternating structure. Perhaps this is also a reason for the observed maximum rate for an equimolar feed of S_8 and DCP (Figure 12). The linear relationship in Figure 13 shows that the rate of increase of logarithmic viscosity is proportional to X^b, except around $X = 0.5$, where X is the mole fraction of DCP in the feed to start with and b is an empirical constant, positive for X less than 0.5 and negative for X greater than 0.5 at a given temperature. The proportionality does not hold around $X = 0.4$ to 0.6, because of the relatively flat nature of the curve at $X = 0.4$ to 0.6 in Figure 12.

A general exponential equation, the derivation for which is discussed later, has been developed:

$$\eta = \eta_o \exp(a\, X^b\, t), \text{ at constant temperature.}$$

It quantitatively relates the melt viscosity, η, of sulfur-DCP solutions (in centipoise) as a function of the initial feed

composition, X, (the mole fraction of DCP) and time, t, (in hours). η_o, a and b are empirical constants, η_o being the viscosity at t = 0, a is a quantity in the unit of reciprocal time and b a dimensionless number. The assumptions made here are:

1. Newtonian behavior of the sulfur-DCP solutions

2. η_o is dependent on temperature only and not on composition as a first approximation because it is an average value determined individually for X < 0.5 and X > 0.5

3. $\frac{d \log \eta}{dt} = a'X^b$, where $a' = \frac{a}{2.30}$, at constant temperature, which is valid for $0 \leq X \leq 0.5$ and $0.5 \leq X < 1$ with two sets of values for a and b for the above two ranges of values for X.

Experimental results appear to support the above assumptions. The parameters η_o, a and b have been determined using least square calculations based on the experimental data in Figures 9, 10, 11, 12 and 13. The final melt viscosity equations with the range of compositions and temperatures at which they are valid are shown below.

$$\eta_{X<0.5}^{140^\circ C} = 19.46 \exp(11.33\ X^{1.78}t), \quad X = 0 \text{ to } 0.4$$

$$\eta_{X>0.5}^{140^\circ C} = 2.50 \exp(0.16\ X^{-4.64}t), \quad X = 0.6 \text{ to } 1$$

$$\eta_{X<0.5}^{155^\circ C} = 38.06 \exp(251.66\ X^{2.42}t), \quad X = 0 \text{ to } 0.2$$

Figure 9: A semi-logarithmic plot of viscosity vs. time for the sulfur – <u>endo</u>-dicyclopentadiene (DCP) solutions at 140°C for the composition of DCP mole fraction, X = 0–50%.
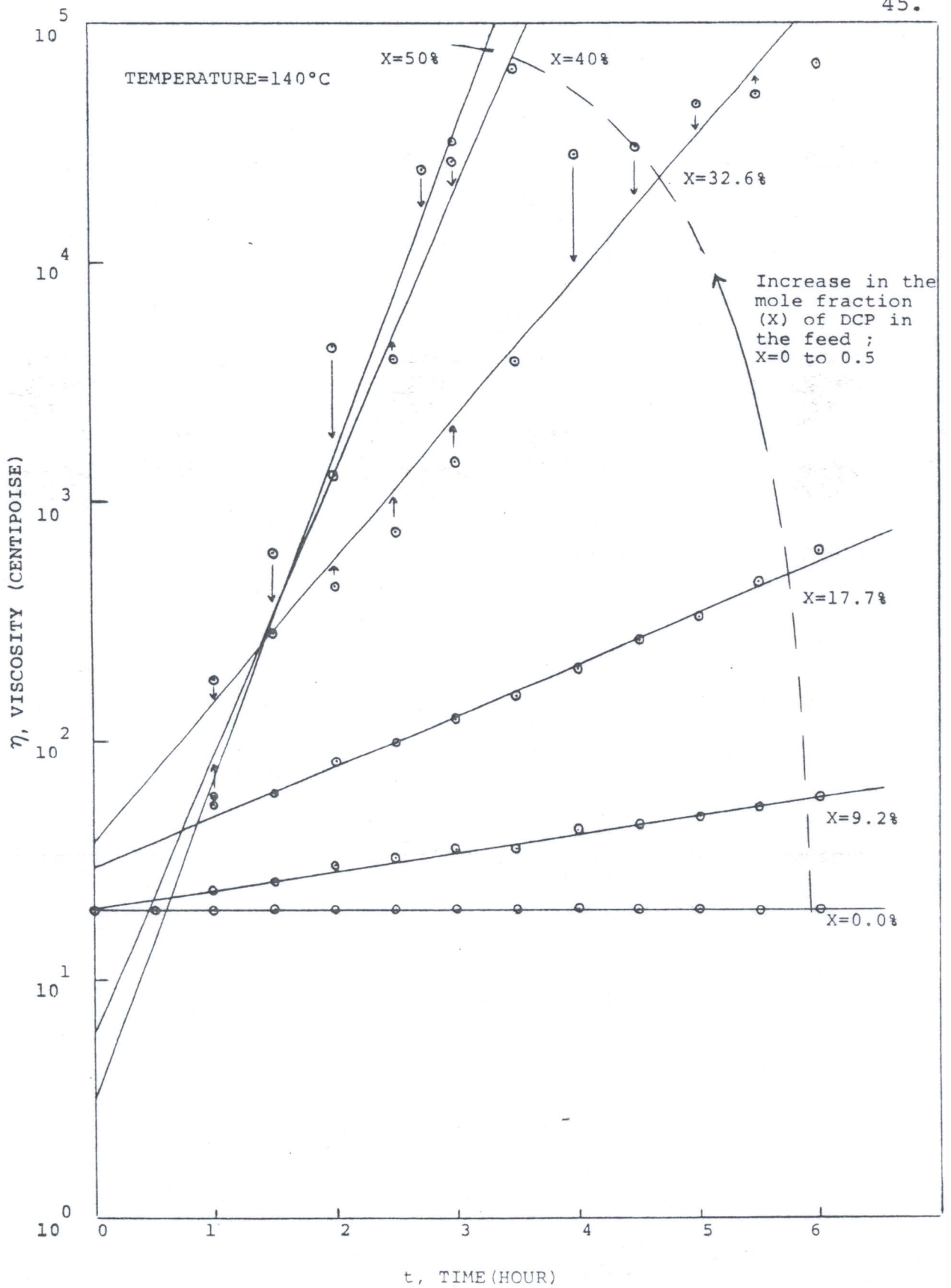
Figure 10: A semi-logarithmic plot of viscosity vs. time for the sulfur - _endo_-dicyclopentadiene (DCP) solutions at 140°C for the composition of DCP mole fraction, X = 50-100%.

Figure 11: A semi-logarithmic plot of viscosity vs. time for the sulfur - _endo_-dicyclopentadiene (DCP) solutions at 155°C for the compositions of DCP mole fraction, X = 0-17.7%.
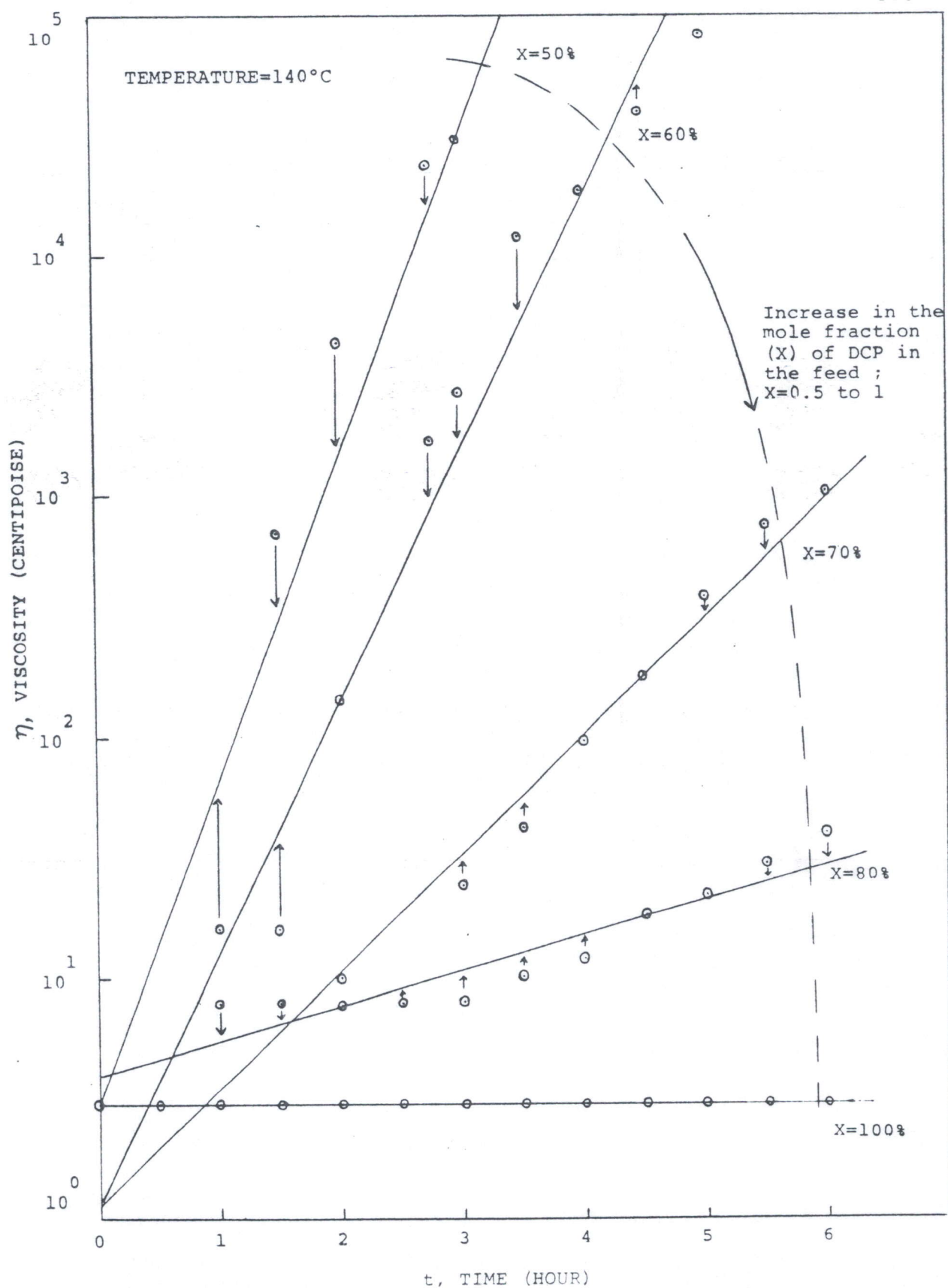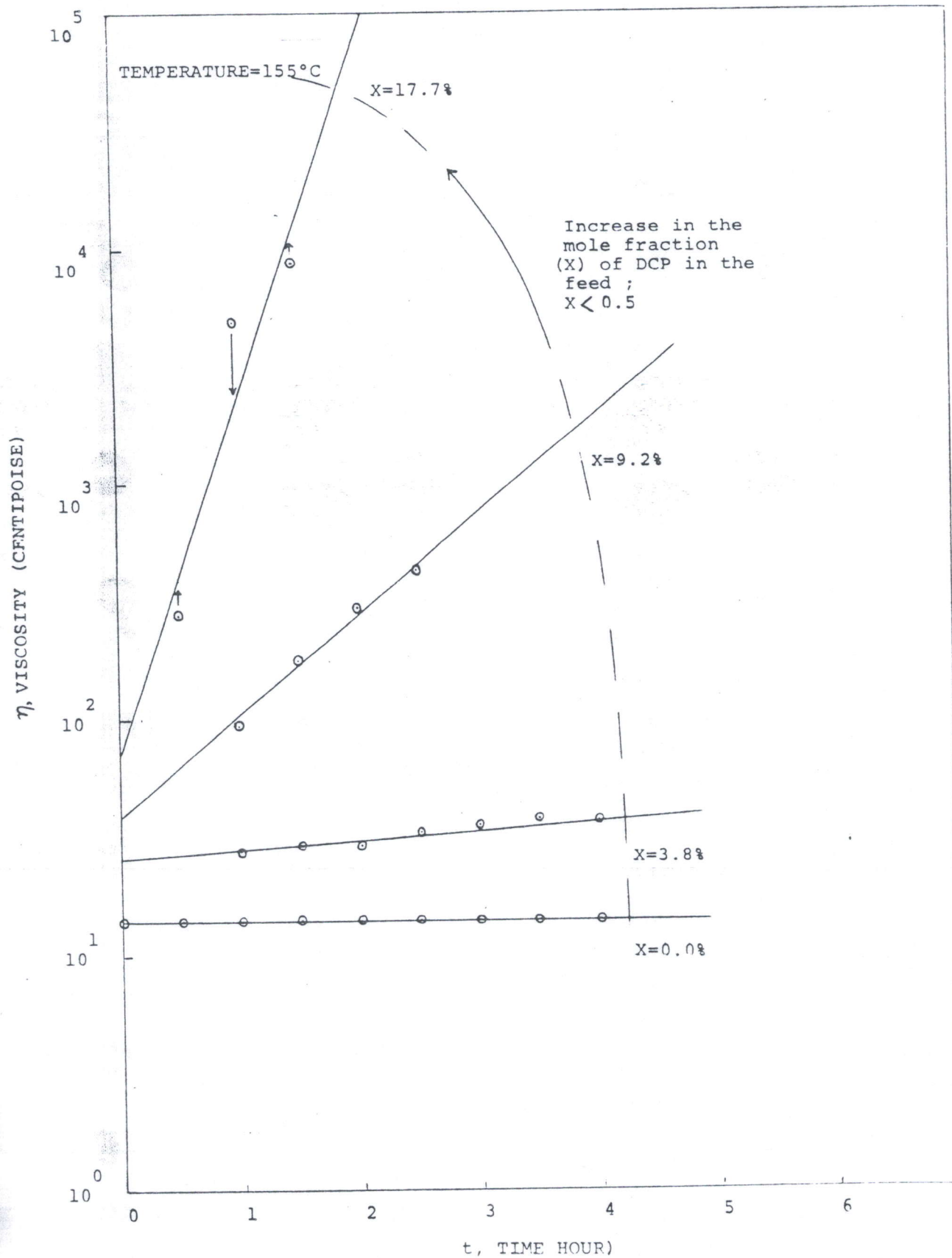
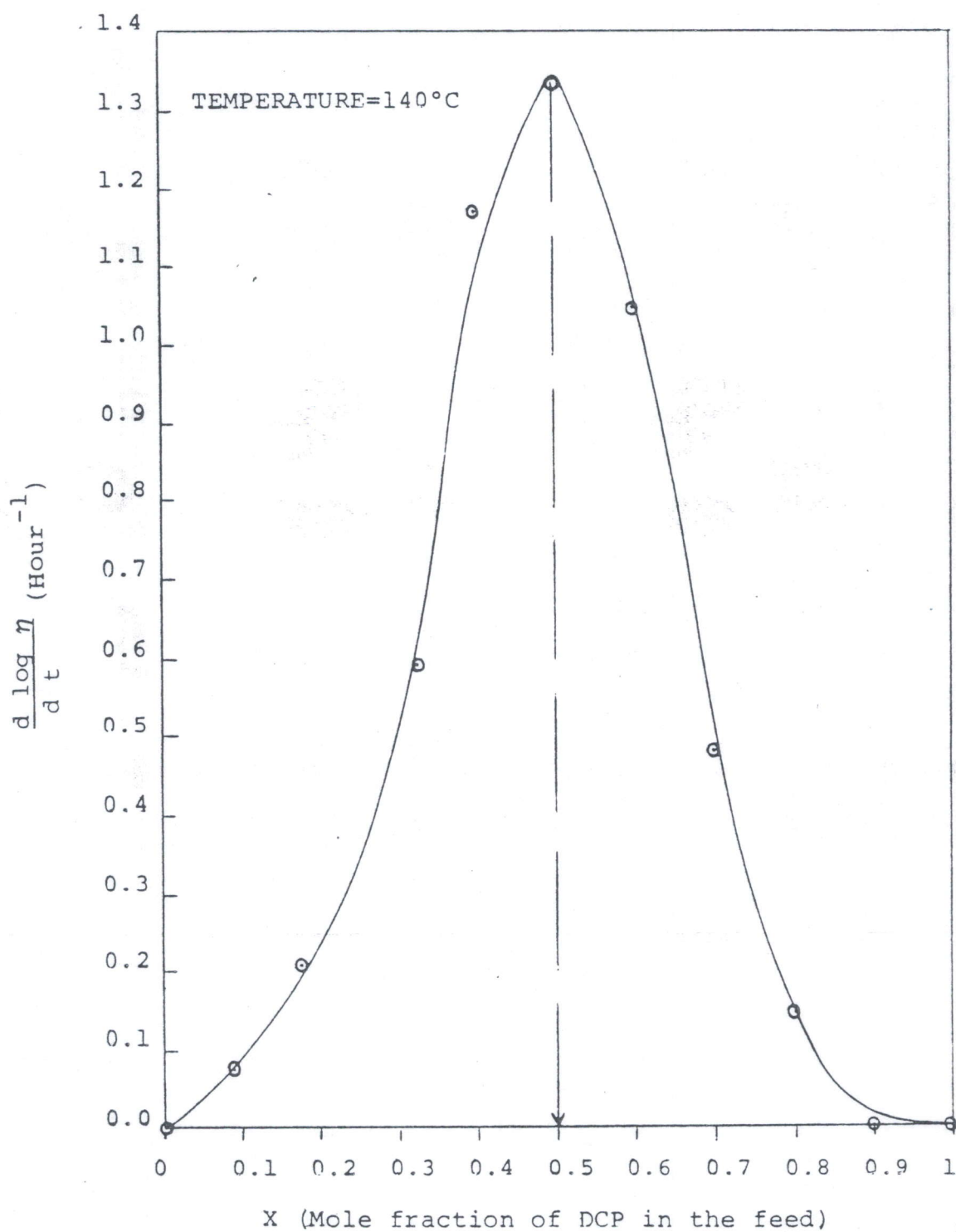Figure 12: A plot of the rate of increase of logarithmic viscosity of sulfur - endo-dicyclopentadiene (DCP) solutions vs. the feed composition in mole fractions of DCP at 140°C.
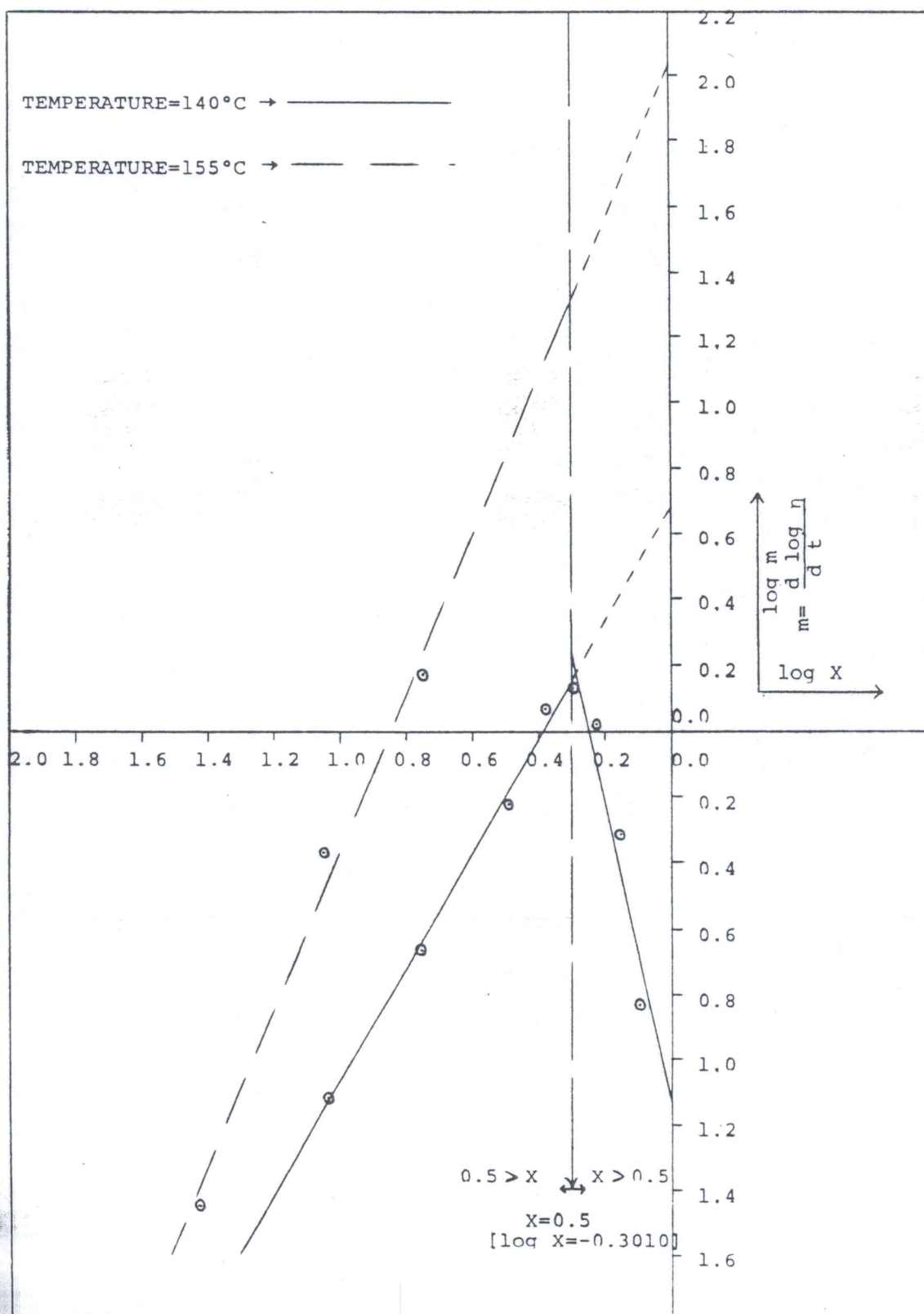
Figure 13: A double-logarithmic plot of the rate of increase of logarithmic viscosity of sulfur - <u>endo</u>-dicyclopentadiene (DCP) solutions vs. the feed composition in mole fractions of DCP; (————) at 140°C and (—— —) at 155°C.

The Melt Viscosity Equation for Sulfur-DCP Solutions:

An assumption is made that the sulfur-DCP solution is a Newtonian fluid, i.e., the viscosity measured by the Brookfield viscometer is independent of the spindle speed of the viscometer, which is related to shear rate. The linear plots of log(viscosity) vs. time (Figures 9, 10 and 11) give give the following equation (1) for a given sulfur-DCP composition at a given temperature:

$$\log_{10} \eta = mt + \log_{10} \eta_o'$$ (1)

where η is the viscosity in centipoise at time t in hours, η_o' is the viscosity at t = 0, and m is the slope, $d \log_{10} \eta / dt$.

An average value of η_o',s of the different compositions (for mole fractions of DCP < 0.5 and > 0.5) at a given temperature can be considered to be independent of composition as a first approximation, and is denoted by η_o. Substituting η_o in Eq.(1) gives Eq. (2):

$$\log_{10} \eta = mt + \log_{10} \eta_o$$ (2)

or

$$\eta = \eta_o \exp(2.30 \, mt)$$ (3)

An assumption is made that m is related to the mole fraction of DCP in the feed, X, at constant temperature by Eq. (4):

$$m = a' \, X^b$$ (4)

where a' and b are empirical constants dependent on temperature only, b a dimensionless number positive for $0 \leq X \leq 0.5$ and

negative for $0.5 \leq X < 1$, and a' in the unit of time^{-1}.

Eq. (4) can be written as Eq. (5):

$$\log_{10} m = b \log_{10} X + \log_{10} a' \qquad (5)$$

The linear plots of log m vs. log X at 140°C and 155°C for $X < 0.5$ and $X > 0.5$ in Figure 13 shows the validity of the above assumption, Eq. (4), except around $X = 0.4$ to 0.6. Eq. (4) is not expected to hold in the region of about $X = 0.4$ to 0.6 because of the relatively flat nature of the curve around $X = 0.4$ to 0.6 in Figure 12.

Therefore, the melt viscosity of sulfur-DCP solutions at a given temperature is a function of composition and time only and can be represented by Eq. (6) by substituting Eq. (4) in Eq. (3):

$$\eta = \eta_0 \exp(2.30 \ a' \ X^b \ t) \qquad (6)$$

If

$$a = 2.30 \ a' \qquad (7)$$

then the general melt viscosity equation of sulfur-DCP solutions is given by Eq. (8):

$$\eta = \eta_0 \exp(a \ X^b \ t), \text{ at constant temperature} \qquad (8)$$

Effect of Dodecyl Polysulfide as a Viscosity Suppressant for the Sulfur-DCP System:

Diehl's previous studies of the dicyclopentadiene-modified sulfur system appears to indicate that the search for viscosity suppressants or regulators is important because progress in this field will considerably broaden the use of

Table 7.

The Effect of Dodecyl Polysulfide (DDPS) on the Sulfur-endo-dicyclopentadiene (DCP) System as a Viscosity Supressor

Composition of S_8: DCP: DDPS		Melt Viscosity Behavior at 140°C				Properties of the materials at ambient temperature made from 6 hrs. reaction time at 140°C
By Mole	By Weight	Viscosity, η (centpoise), at the t th time (hour)			The rate of increase of logarithmic viscosity, $\dfrac{d \log_{10}\eta}{dt}$ (hour^{-1})	
		$t=0$	$t=3$	$t=6$		
1:1:0.0	S → 66.0% DCP → 34% DDPS → 0.0%	8	3.1×10^4	$\gg 10^5$ Too high to measure	1.34	Dark brown hard brittle solid
1:1:0.1	S → 58.9% DCP → 30.4% DDPS → 10.7%	14	6.0×10^2	4.2×10^3	0.39	Dark brown soft flexible solid
1:1:0.2	S → 53.2% DCP → 27.4% DDPS → 19.3%	14	3.5×10	7.0×10	0.12	Dark brown very high viscous liquid

Some experimentally determined data are summerized in Table 7.
An equimolar composition of S_8:DCP has been chosen here because
the rate of increase of viscosity is maximum for this
composition. The properties of the resulting materials,
(Table 7), vary depending on the amount of DDPS used. It has
also been observed that there is no indication of sulfur
crystallization in these materials.

4.1.3.2. Behavior of Surface Tension of Sulfur-Dicyclopentadiene (DCP) Solutions:

The behavior of the surface tension of liquid sulfur-
DCP solutions as the copolymerization reaction proceeds is of
interest as these systems are used as sprayable coatings. The
bubble pressure method is an experimentally simple method and
a good procedure for surface tension measurements of viscous
liquids[44]. Fanelli's measurements on the surface tension of
sulfur over the entire liquid range are considered to be the
most accurate[41,45]. He used the Sugden's double capillary
modification of the maximum bubble pressure method[27].
Recently the surface tension of sulfur has been determined in
an atmosphere of sulfur vapor in the temperature range, $120^{\circ}C$
to $435^{\circ}C$, by using the large drop method[46]. Surface tension
measurements have been carried out in the present study on
sulfur-DCP solutions using the former method because of its
simplicity[45].

The surface tension of sulfur and DCP at $140^{\circ}C$ are
determined to be 69.0 and 21.9 dynes cm^{-1} respectively. The

Table 8.

Surface Tensions of Sulfur-endo-dicyclopentadiene (DCP)
Solutions Containing 5 Weight % (or 9.2 mole %)
DCP at 140°C.

Time (Hour)	Viscosity (Centipoise)	Surface Tension (Dynes cm^{-1})
0	16	62.7
1	24	62.7
2	30	65.9
3	35	70.6
4	42	73.7
5	47	76.8

Table 9.

Surface Tension of Sulfur-endo-dicyclopentadiene (DCP)
Solutions Containing 20 Weight % (or 32.6 mole %)
DCP at 140°C.

Time (Hour)	Viscosity (Centipoise)	Surface Tension (Dynes cm^{-1})
0	26	50.2
1	184	75.3
2	430	84.7
3	1430	Not possible to measure

surface tension of sulfur-DCP solutions at 140°C with two
compositions are shown in Tables 8 and 9. Surface tension
has been determined as a function of time and the melt viscosity
of the solutions are shown along with the surface tension.
The data clearly indicates that as the viscosity increases,
surface tension also increases with time, and the higher the
rate of viscosity increase, the higher the rate of surface
tension increase. It has been shown for silicone polymers
that as the viscosity of silicone polymers increases due to an
increase in molecular weight, the surface tension increases[47].
Therefore it indicates that the molecular weight of the
polymeric polysulfides formed in the sulfur-DCP system
increases with time, which is in agreement with the results of
Blight, et al.[31].

It can be concluded that the behavior of melt viscosity
and surface tension of liquid sulfur-DCP solutions appear to
support a step-growth mechanism for polymerization.