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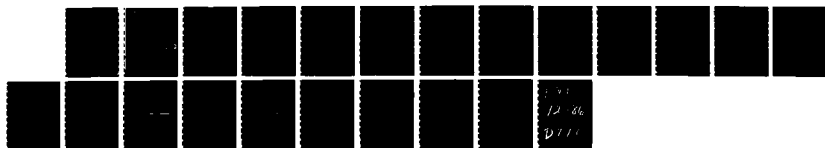| 4. TITLE (and Subtitle) | 5. TYPE OF REPORT & PERIOD COVERED |
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# THERMAL POLYMERIZATION OF ISOMERIC DODECADIENDIYNDIOLS

by

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## INTRODUCTION

C Triple bond C

Recently, the polymerization of acetylenic compounds having two or more acetylene units, $R-(C\equiv C)_n-R'$, has attracted much attention and numerous reports have been published. In the case of diacetylenes, n=2, the majority of studies are concerned with the unique topochemical polymerization in crystalline states. However, little has been studied on the thermal behavior of these polyacetylenic compounds, except for diphenyl diacetylenes, although it is known that many of them simply undergo polymerization on heating. When n is greater than four and R=H, the compounds become unstable and in many
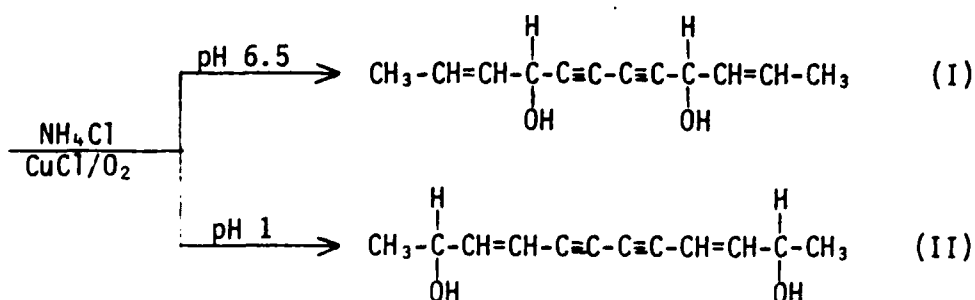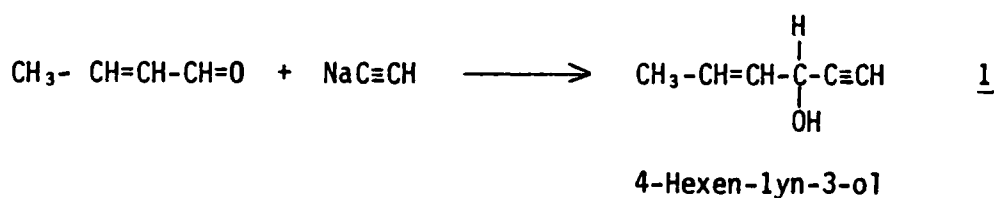
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cases it is difficult to prevent their polymerization on standing. Jones and his coworkers have synthesized many polyacetylenic compounds[2] including those occurring naturally in plants of Compositae family.[3] These polyacetylenes contain four or five conjugated acetylenic units linked to the terminal vinyl groups and are reported to be dangerously unstable. Nakagawa[4] has prepared diphenyltetraacetylene, which is stable in the dark. Korshak et al.[5] have claimed that a polyyne with a structure $H-(C{\equiv}C)_n-H$, and stable up to $2300°C$ was obtained by the oxidative dehydropolycondensation of acetylene. Although the relationships between stability and structure are not yet clear, all of these compounds are interesting as potential heat resisting materials with high carbon contents.

## RESULTS AND DISCUSSION

We prepared 2,10-dodecadien-5,7-diyn-4,9 diol (I) and 3,9-dodecadien-5,7-diyn-2,11-diol (II), which have two acetylene units and two olefinic groups, by the method reported by Jones et al.[6] as shown below, and their thermal reactions were studied in this work.

$$CH_3-CH{=}CH-CH{=}O \;+\; NaC{\equiv}CH \longrightarrow CH_3-CH{=}CH-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-C{\equiv}CH \qquad \underline{1}$$

4-Hexen-1yn-3-ol

$$\xrightarrow{\text{pH } 6.5} CH_3-CH{=}CH-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-C{\equiv}C-C{\equiv}C-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-CH{=}CH-CH_3 \qquad (I)$$

$$\frac{NH_4Cl}{CuCl/O_2}$$

$$\xrightarrow{\text{pH } 1} CH_3-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-CH{=}CH-C{\equiv}C-C{\equiv}C-CH{=}CH-\overset{\displaystyle H}{\underset{\displaystyle OH}{C}}-CH_3 \qquad (II)$$

Jones et al. obtained the (I) in 90 percent yield when the coupling reaction was carried out at pH 6.5, whereas (II) was obtained in high yield at pH 1. They reported that (I) rearranges to (II) in the presence of acid, and the melting points of (I) and (II) were cited as $125^O$ and $95^O$ respectively. In this work, the same isomers were obtained as described above. Differential scanning calorimetry of (I) and (II) showed melting temperatures of $124.5^O$ and $93.5^O C$ respectively (Figure 1), whereas the broad exotherm at $160-240^O C$ may be due to beginning of decomposition.

Characterization of both (I) and (II) was done by $^1H$ and $^{13}C$ NMR and IR spectroscopy techniques. Figure 2 shows proton NMR spectra of (I) and (II). Olefinic protons $\alpha$ to C≡C in (II) gave a doublet at 5.67 ppm (J=16.9 Hz), whereas $\beta$ protons gave doublet of doublet centered at 6.23 ppm (J=15.75 Hz), and a multiplet was observed at 4.19 ppm assignable to -CH(OH). Both in (I) and (II), the methyl groups resonate as doublet (J=6.25 Hz), but the peak position in (I) was shifted considerably appearing at 1.71 ppm compared to 1.11 ppm for the corresponding resonance in (II). Such a shift may be explained through the olefinic group next to the methyl group in (I). Hydroxyl groups showed as broad peak, and peak area integration was perfect as expected from the structures of (I) and (II).

The C-13 NMR of (I) and (II) are presented in Figures 3 and 4 respectively. The C-13 chemical shifts for 1 and (I) are consistent with those previously observed[7,8] allowing for solvent-solute effects and instrument variability. For comparison, the chemical shifts for 1 are also included (see Experimental section). Procedures which are common[9] in C-13 such as off-resonance decoupling multiplicity pattern, chemical shift, data from model compounds, etc.

were used for the resonance assignment. These procedures readily permit the
various types of carbons to be distinguished. A comparison between C-13 NMR
spectra of (I) and its monoenynol precursor, 4-hexen-1yn-3ol $\underline{1}$, revealed
that the chemical shift pattern evident for (I) is very reminiscent of that
observed for $\underline{1}$, for example, the methyl and carbinol carbon resonances are
very similar. This close analogy also applies to chemical shifts of olefinic
carbons, but the acetylenic carbons in (I) are shifted by ca.4 ppm compared
with the corresponding carbon in $\underline{1}$.[8]

The simple six-line spectrum observed for symmetrical (I) and (II),
derived from six non-equivalent types of carbon atoms, can be divided into
three major regions, depending on the hybridization of the carbon. The assign-
ment of SP hybridized carbons of triple bonds was easily made. When two triple
bonds are conjugated, as in (I) and (II), the mutual shielding effect of each
triple bond resulted in the adjacent $\alpha$-sp hybridized carbons moving upfield.
In (I), the exterior sp hybridized carbons are ca.6 ppm downfield of the
interior SP hybridized carbons, while for the (II) the relative difference in
shifts is ca.12 ppm. The greater difference between the interior and exterior
acetylenic carbons in (II) is presumably due to substituent effects. $SP^3$
hybridized methyl and carbinol carbons for both (I) and (II) were observed in
the expected range of chemical shifts, and peaks showed the expected multiplic-
ity. $SP^2$ hybridized olefinic carbons in (I) appeared as doublets at 128.99
and 126.09 ppm as it should for any simple olefin, whereas (II) being conjugated
alkenyne, the triple bond shields the $\alpha$-olefinic carbon by ca.23 ppm but deshields
the $\beta$-olefinic carbon by ca.17 ppm relative to the corresponding alkene.[10]
Therefore, olefinic carbons of (II) appeared as doublets distinctly separated at

150.77 and 105.35 ppm. Thus, the chemical shifts and multiplicity of all carbons in (I) and (II) are consistent with the structure described.

The IR spectrum of (I) (Figure 5) showed O-H stretch (> 3250 $cm^{-1}$), C-O stretch of secondary alcohol with di-$\alpha$-unsaturation (994 $cm^{-1}$) together with olefinic C-H stretch (3050 $cm^{-1}$), and a weak band due to disubstituted unconjugated trans C=C stretch (1672 $cm^{-1}$). Similar absorptions were seen for (II), including a weak band at 1633 $cm^{-1}$ assigned to the C=C stretching vibration of internal symmetrical disubstituted olefin. Vibrations due to C≡C stretch in the range of 2260-2190 $cm^{-1}$ were almost absent, due to the symmetrical nature of (I) and (II).

Table I shows the conditions of polymerization of (I) and (II) and the characteristics of polymers derived. The results of elemental analysis indicate that there was no appreciable difference in the composition before and after polymerization at 130° or 150°C. Apparently, no decomposition and/or dehydration occurred during the polymerizations conducted at lower temperatures. The polymers obtained at or below 150°C were reddish-brown and those obtained at 500°C were shiny black. Yields of methanol insoluble polymers ranged from 52-79 percent, depending on polymerization conditions and monomer. Typical IR spectrum of polymer (Figure 5) showed broad bands with increased intensity of the absorptions due to conjugated C=C stretching vibrations as compared to that of (I) or (II), suggesting that polymerization proceeds via diacetylenic units, thereby increasing the conjugation in resulting polymer. At the initial stage of polymerization, the polymer was still soluble in dimethylformamide and brittle threads could be drawn from its

molten state, but the longer periods of polymerization gave insoluble and in-
fusible polymers, probably due to increased molecular weight and/or crosslinking.
The gel permeation chromatograph of soluble polymers gave a molecular weight of
about 1700-2000.

The mass-spectral fragmentation of (I) and (II) at $230^oC$ (Figure 6)
produced $M - 15$ (loss of methyl) as initial fragmentation and hydroxyethyl
part of (II) corresponding to ca.40 percent weight loss observed in TGA of
(II) as shown in Figure 7. Under same conditions, (I) lost little less than
25 percent of its weight up to $200^oC$ due to random scission across olefinic
linkage beside the methyl group loss, as evidenced by corresponding fragmenta-
tion peaks in mass spectrum of (I). Neither (I) nor (II) decomposed appreciably
below $150^oC$ as shown in Figure 7 and Table I, but lost their weight continuously
with increase in temperature, (I) losing its total weight at $800^oC$. On the
other hand, polymers I-500-2 and II-500-2 showed no weight loss below $500^oC$
(Figure 8) and polymer II-500-2 retained ca.50 percent of its weight at $1000^oC$,
while polymer I-500-2 lost its weight completely. These results are not sur-
prising because of an extended enyne conjugation in (II) yielding more con-
jugated polymer II-500-2 and subsequently more graphitization. Conductivity
measurements support these findings. The electrical conductivity of polymer
II-500-2 was found to be $3.6 \times 10^{-2} \, \Omega^{-1}$, while polymer I-500-2 showed conduc-
tivity of $5 \times 10^{-6} \, \Omega^{-1}$ under the same conditions. Polymerization of (I) and
(II) at $400^oC$ for four hr in a sealed tube gave dark-brown polymers with con-
ductivity of the order of $10^{-9} \, \Omega^{-1}$, indicating that no graphitization took
place at $400^oC$. The nature of conductivity was of electronic character, since
the measurements with direct and an alternate currents gave same results.

Thus, these studies suggest that highly heat-resistent organic materials could be obtained from conjugated acetylenic compounds, preferably having no aliphatic substituents which decompose at lower temperatures.

## EXPERIMENTAL

Synthesis of 4-hexen-1yn-3-ol: $\overset{1}{H}\overset{2}{C}\equiv\overset{3}{C}-CH(OH)-\overset{4}{CH}=\overset{5}{CH}-\overset{6}{CH_3}$: <u>1</u>

The title compound was prepared from crotonaldehyde and acetylene following the procedure reported by Brandsma.[11] Colorless liquid, bp. 49-50°C/10 mm (Lit. 60°C/12 mm) was obtained in 69 percent yields.

NMR: $^1H$ (δ in ppm): 5.9-5.0 (m, 2H), 4.5 (s, 1H), 3.27 (bs, 1H), 2.26 (d, 1H), 1.4 (d, 3H).

$^{13}C$: (δ in ppm): 129.46 (d, $J_{CH}$ = 146 Hz, $C_4$), 128.28 (d, $J_{CH}$ = 162 Hz, $C_5$), 83.11 (S, $C_2$), 73.58 (S, $C_1$), 61.79 (d, $J_{CH}$ = 149 Hz, $C_3$), 16.98 (q, $J_{CH}$ = 126 Hz, $C_6$)

where s = singlet, d = doublet, dd = doublet of doublet, q = quartet, bs = broad singlet, m = multiplet.

Synthesis of dodeca-2,10-dien-5,7-diyn-4,9-diol (I): $\overset{1}{H_3}C-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH}(OH)-\overset{5}{C}\equiv\overset{6}{C}-)_2$ and dodeca-3,9-dien-5,7-diyn-2,11-diol (II): $(\overset{1}{H_3}C-\overset{2}{CH}(OH)-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{C}\equiv\overset{6}{C}-)_2$ was performed as reported by Jones and coworkers.[6] Each product was recrystallized from benzene to give sharp melting crystalline (I), mp. 124.5-125°C and (II) mp. 93.5-95°C.

(I): Elem. Anal. Calcd. for: $C_{12}H_{14}O_2$: C, 75.79; H, 7.37%.

Found: C, 75.76; H, 7.41%.

NMR: $^1H$ (δ in ppm): 5.80 (m, 1H), 5.53 (m, 2H), 4.79 (bs, 1H), 1.71 (d, J = 6.5 Hz, 3H).

$^{13}C$: ($\delta$ in ppm): 128.99 (d, $J_{CH}$ = 175 Hz, $C_3$), 126.09 (d, $J_{CH}$ = 176 Hz, $C_2$), 79.02 (s, $C_5$), 67.33 (s, $C_6$), 60.55 (d, $J_{CH}$ = 146 Hz, $C_4$), 16.04 (q, $J_{CH}$ = 127 Hz, $C_1$).

(II): Elem. Anal. Calcd. for: $C_{12}H_{14}O_2$: C, 75.79; H, 7.37%.

Found: C, 75.78; H, 7.36%.

NMR: $^1H$ ($\delta$ in ppm): 6.23 (dd, J = 15.75 Hz, 1H), 5.67 (d, J = 16.9 Hz, 1H), 4.64 (bs, 1H), 1.11 (d, J = 6.5 Hz, 3H).

$^{13}C$: ($\delta$ in ppm): 150.77 (d, $J_{CH}$ = 158 Hz, $C_3$), 105.35 (d, $J_{CH}$ = 164 Hz, $C_4$), 78.70 (s, $C_5$), 72.87 (s, $C_6$), 65.49 (d, $J_{CH}$ = 146 Hz, $C_2$), 21.89 (q, $J_{CH}$ = 127 Hz, $C_1$).

## Polymerization

The polymerizations performed at $130^o$ and $150^oC$ were carried out under inert atmosphere in a tube immersed in an oil bath for fixed intervals of time. Polymers were isolated by pouring contents in methanol. When no methanol in-soluble polymer was obtained, the contents were dissolved in acetone and pre-cipitated in hexane. Polymers were purified by reprecipitation method. Heating at $400^o$ and $500^oC$ was made in a Pyrex sealed tube under vacuum. After polymeriza-tion, the dark-colored products were ground to powder and washed with methanol to get dark-brown or black shiny materials.

## Analytical Procedures

Differential scanning calorimetry was performed on a Perkin-Elmer DSC 1B at a heating rate of $20^oC$/min under steady flow of nitrogen. The IR spectra were recorded on a Perkin-Elmer 983 IR spectrometer as KBr pellets. Proton and C-13 NMR spectra were recorded on a Varian EM-360 60 MHz $^1H$

spectrometer and Bruker WM 250 FT spectrometer with a carbon-13 frequency of 62.9 MHz respectively, for ten percent solutions in a mixture of $CDCl_3$-$d_6DMSO$ with TMS as an internal standard. Mass spectra were taken on a Hewlet-Packer Model -5985 mass spectrometer with GC/MS system. Samples were heated at 150-230°C, keeping temperature of the ionization chamber at 230°C and ionization potential of 70 eV.

The molecular weights of soluble polymers were determined by gel permeation chromatography (GPC) with DuPont Zoebax PSM-300S, PSM-60S and IBM 10 μm pore size columns in dimethylformamide at flow rate of 1 ml/min, using Water Associate differential refractometer R403 as detector and standard polystyrene calibrated curve. Thermogravimetric analysis (TGA) was performed on DuPont thermo-balance Model 951 at a heating rate of 10°C/min under nitrogen atmosphere. For the conductivity measurements, polymer samples were ground to fine powders and compressed in a teflon ring between tungsten metal rods to get 0.5 mm thick disk of five mm diameter. Resistance of this sample was measured using a Keithley Model 614 Electrometer at 26°C.

## ACKNOWLEDGMENT

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TABLE I

Polymerization of (I) and (II) and Polymer Characteristics

| Monomer | Polymerization Conditions | | yield[a] % | code | Elemental Analysis % (Found) | | |
| | at ($^o$C) | for (hr) | | | C | H | O |
| --- | --- | --- | --- | --- | --- | --- | --- |
| I | -- | -- | -- | -- | 75.76 | 7.41 | 16.28 |
| II | -- | -- | -- | -- | 75.78 | 7.36 | 16.84 |
| I | 130 | 20 | -- | I-130-20 | 76.28 | 6.81 | 17.05 |
| I | 150 | 2 | 69 | I-150-2 | 73.51 | 6.60 | -- |
| I | 150 | 40 | 76 | I-150-40 | 76.01 | 6.91 | 16.80 |
| I | 500 | 2 | 54.2 | I-500-2 | 91.65 | 3.33 | 4.29 |
| II | 130 | 20 | 32[b] | II-130-20 | 73.72 | 7.04 | -- |
| II | 150 | 2 | 43[b] | II-150-2 | 75.78 | 6.67 | 16.47 |
| II | 150 | 30 | 79 | II-150-30 | 73.97 | 6.49 | 18.60 |
| II | 500 | 2 | 52 | II-500-2 | 90.40 | 3.25 | 4.48 |

a.  Methanol insoluble polymer.

b.  No methanol insoluble polymer was obtained.  Yield represents polymer
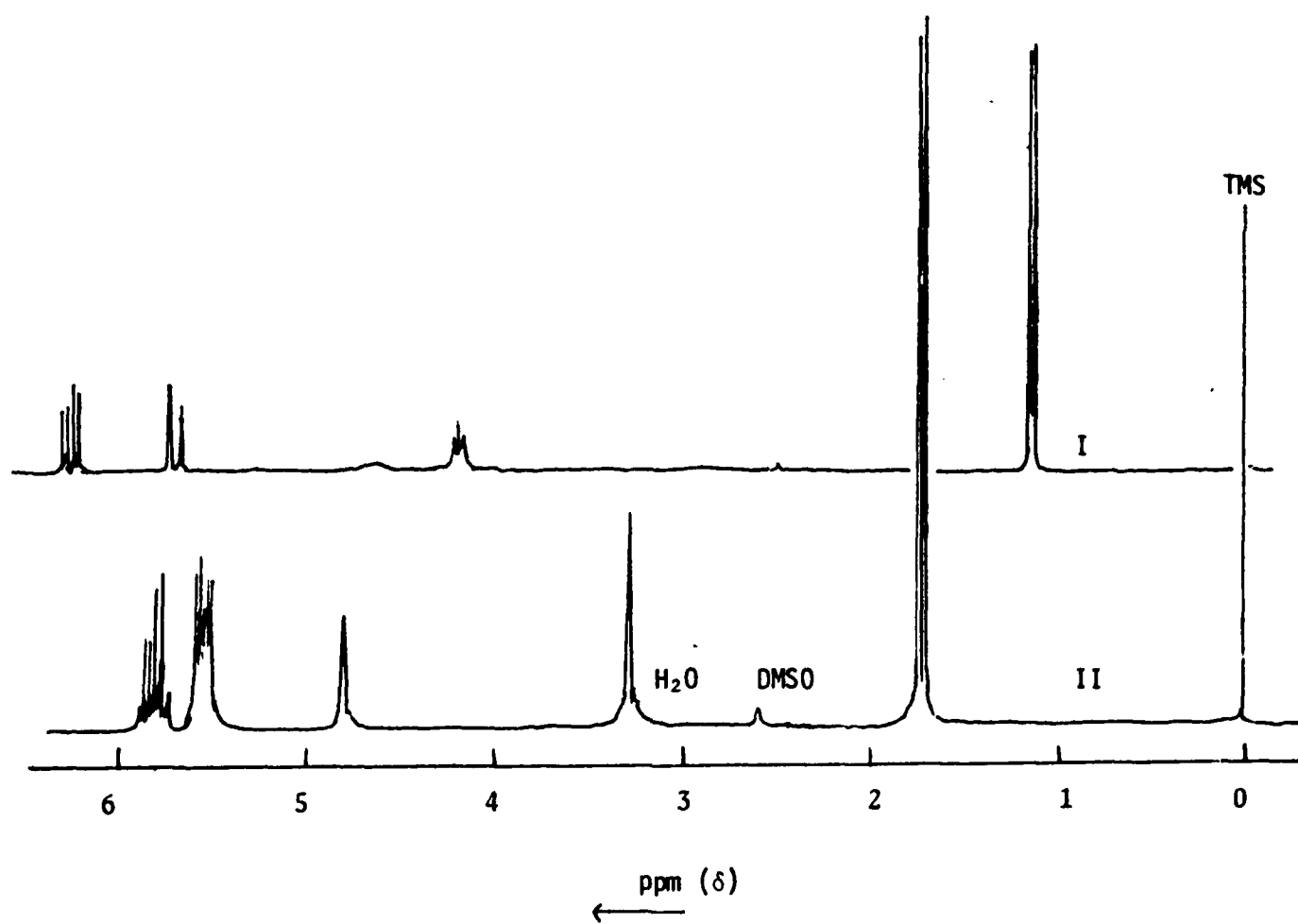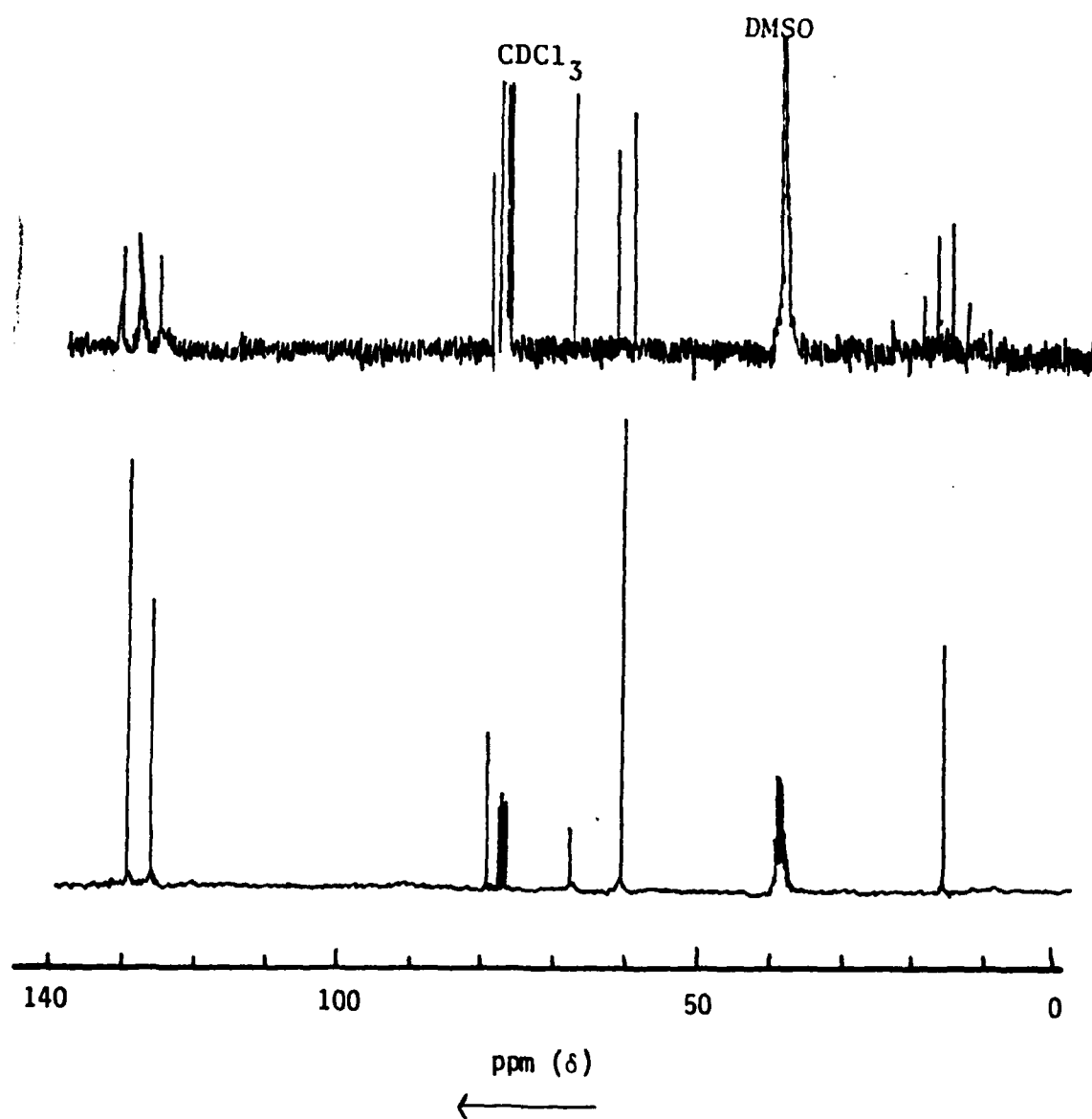obtained by precipitation in hexane from acetone solution.
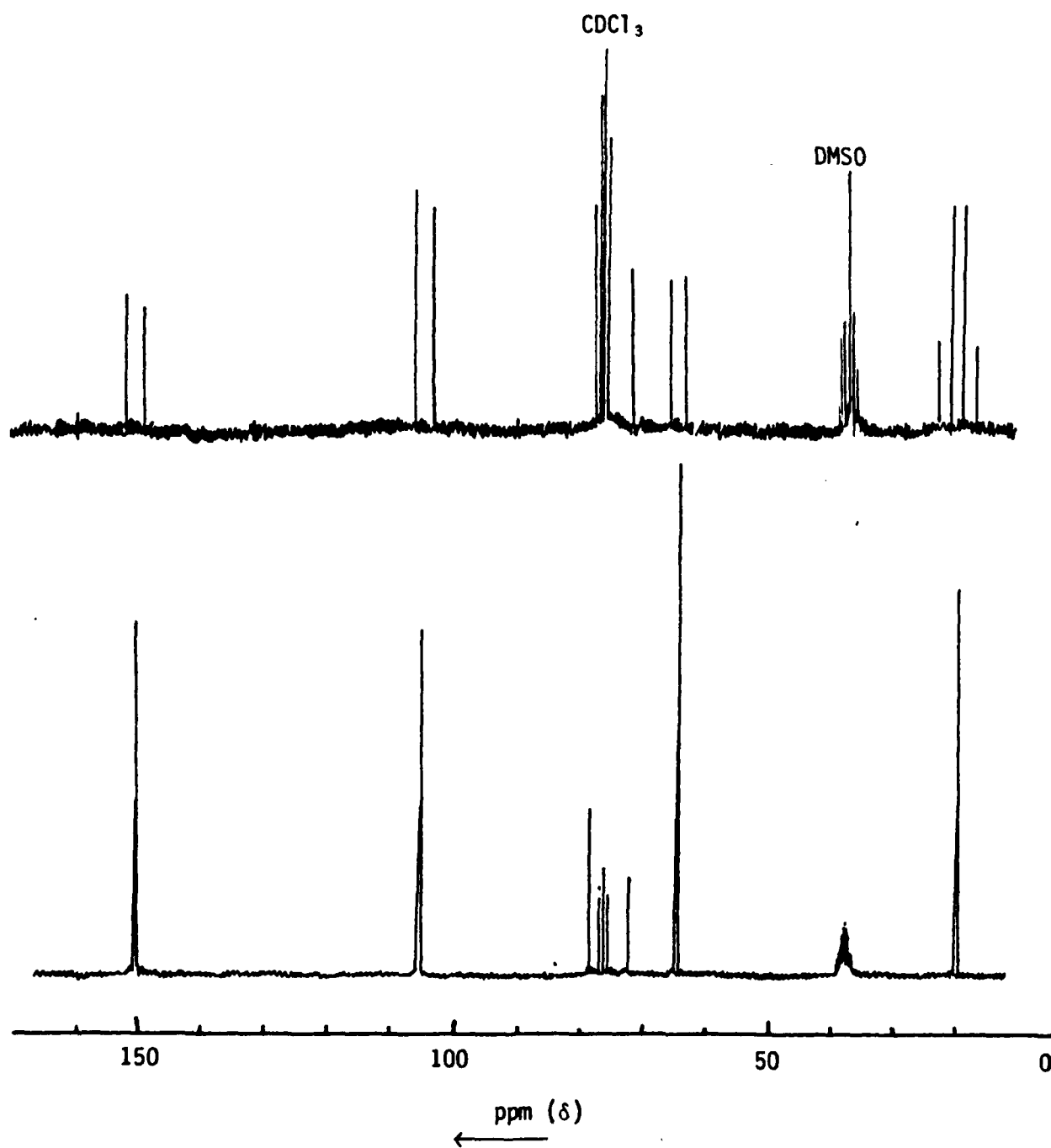
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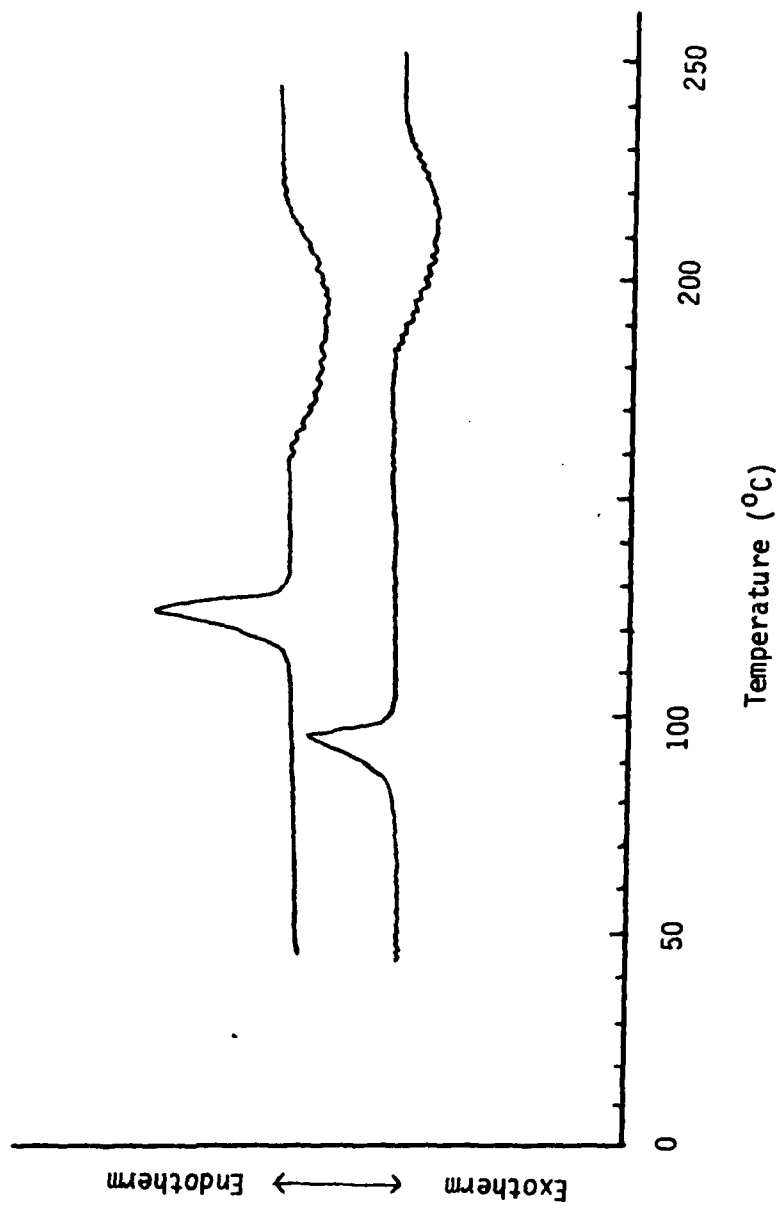


Temperature (°C)

FIGURE 1

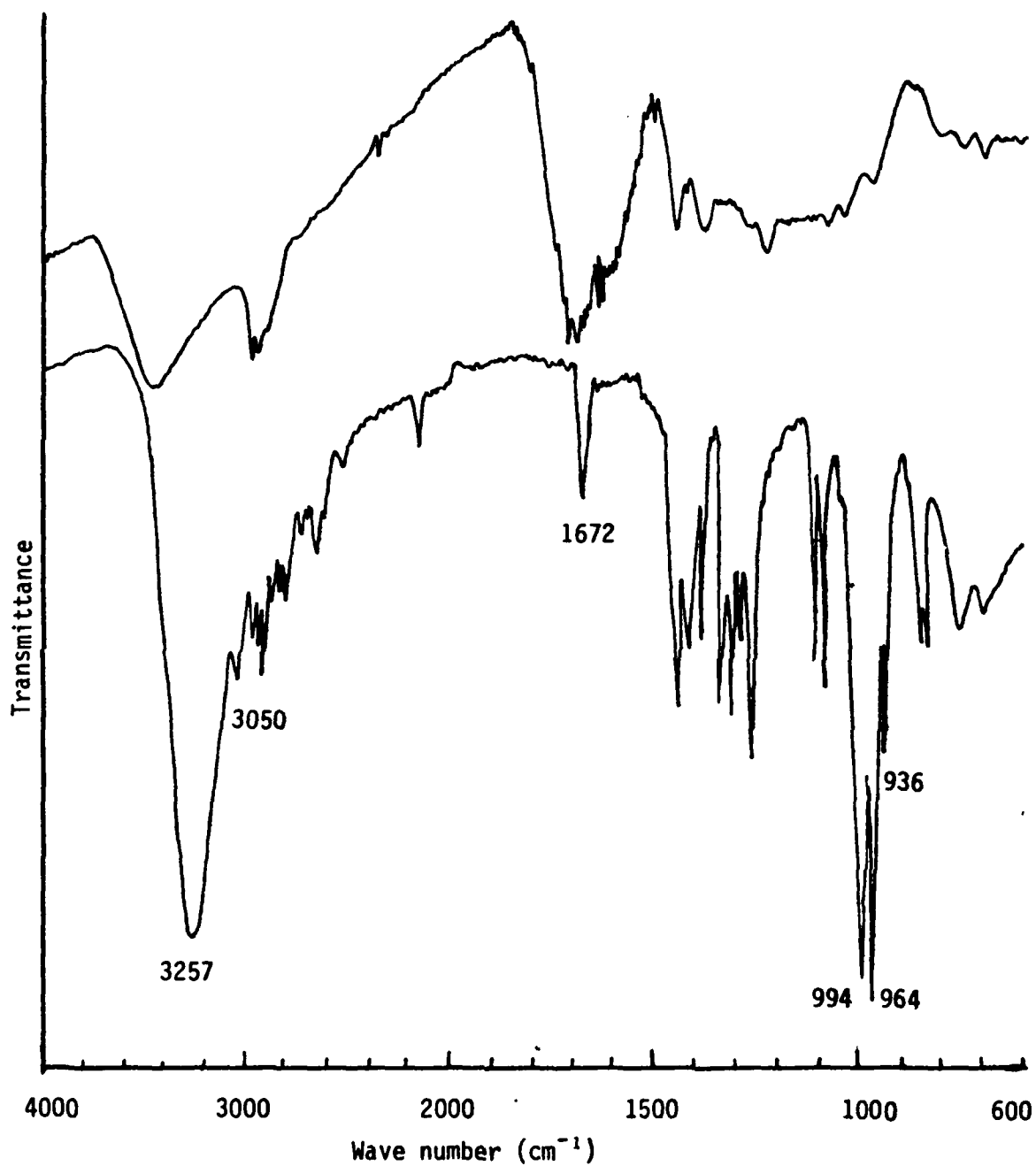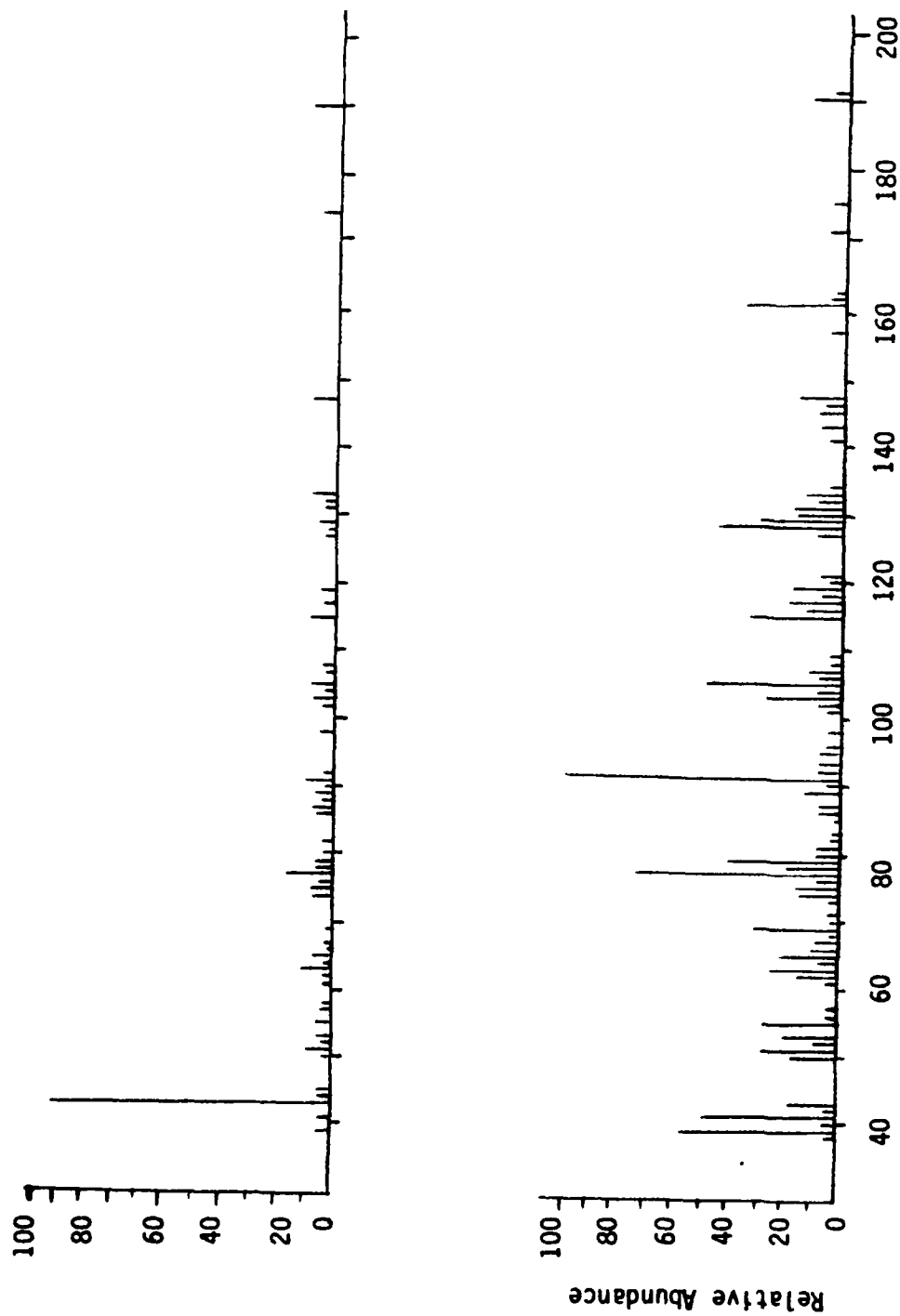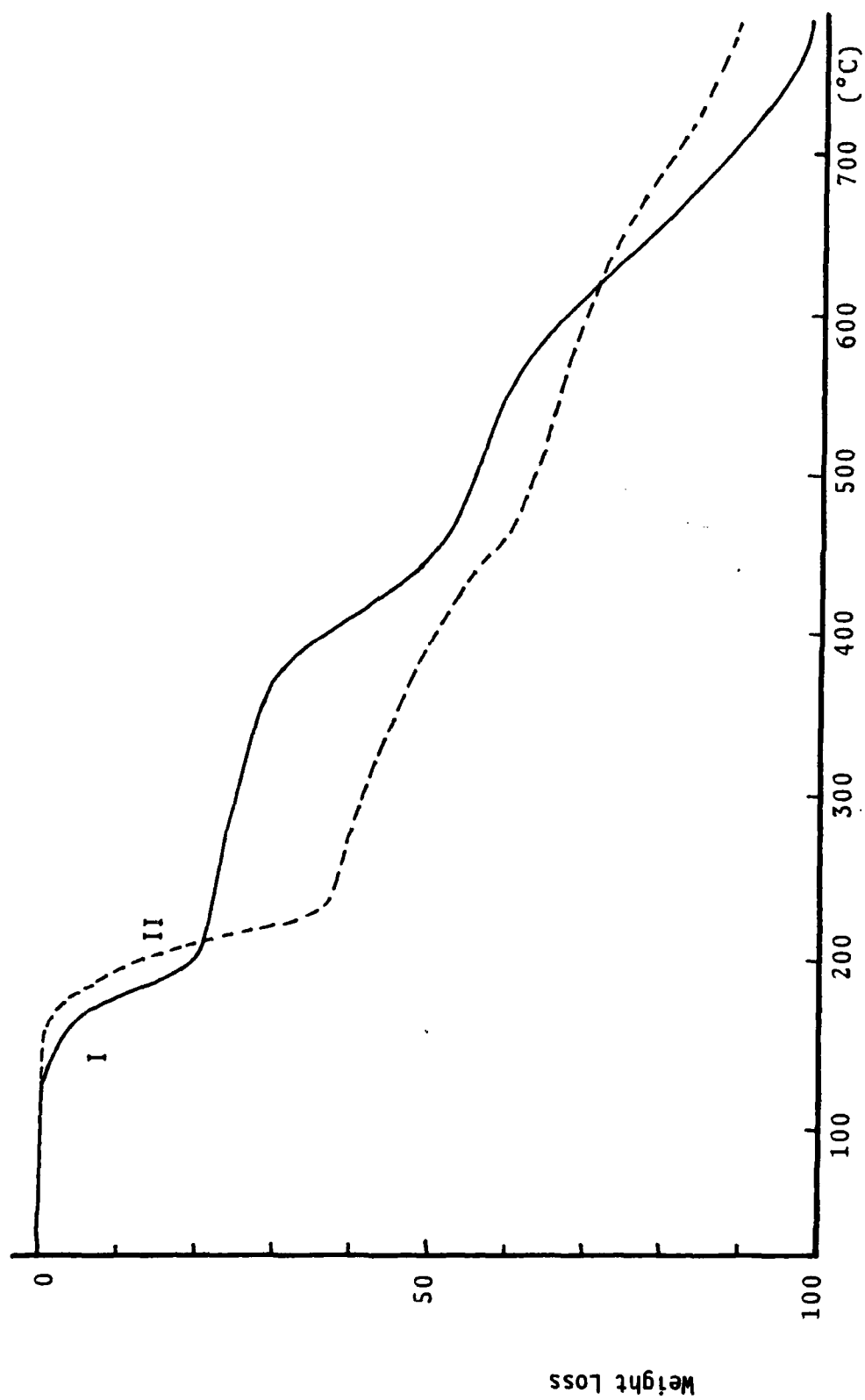FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

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FIGURE 6
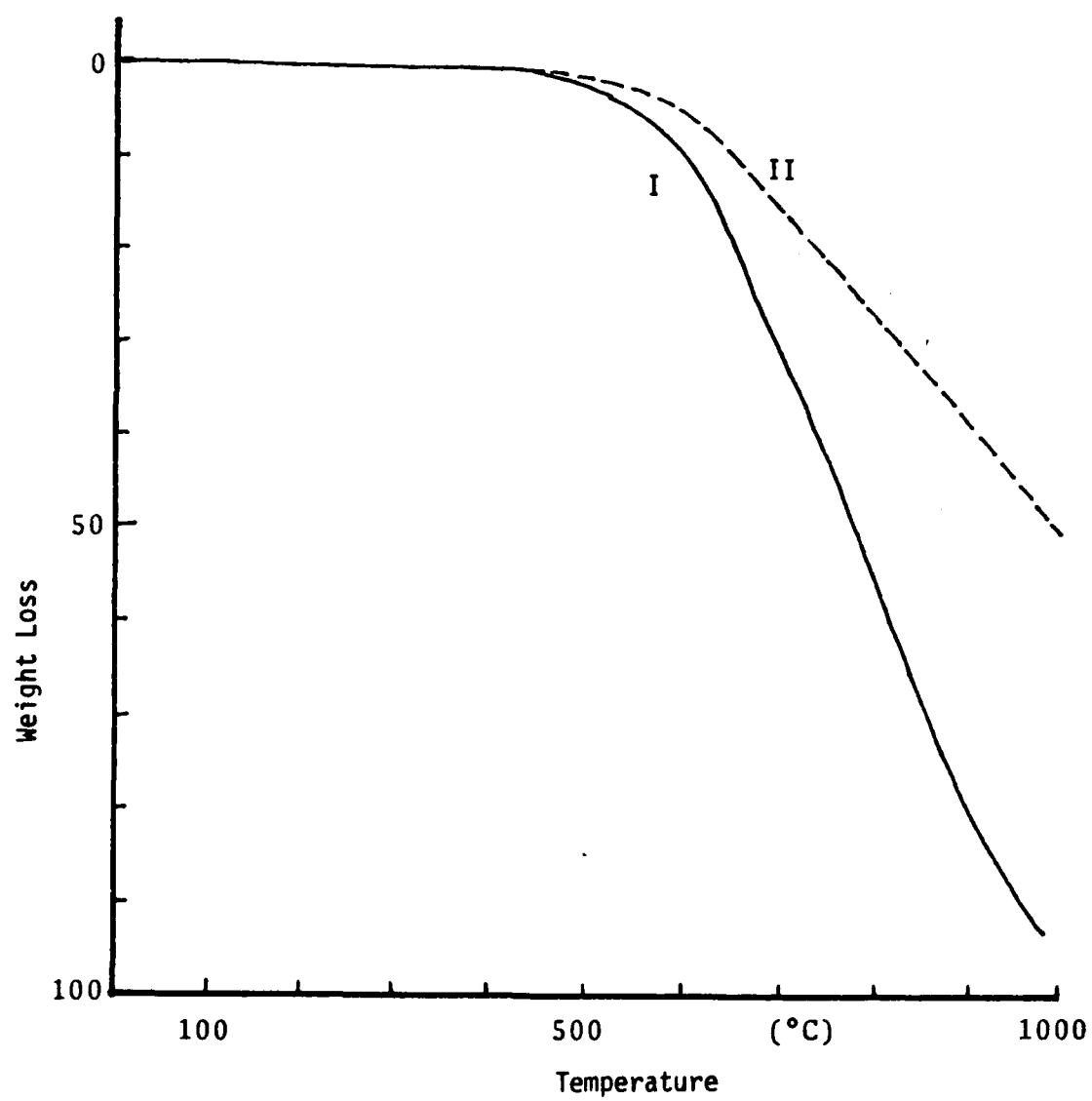
Temperature

FIGURE 7

FIGURE 8

## FIGURE LEGENDS

Figure 1.  DSC curve of (I) and (II).  Heating rate $20^{\circ}$C/min in nitrogen.

Figure 2.  $^1$H NMR spectra of dodeca-2,10-dien-5,7-diyn-4,9-diol (I) and dodeca-3,9-dien-5,7-diyn-2,11-diol (II), in $CDCl_3$-$d_6$ DMSO mixture.

Figure 3.  $^{13}$C NMR spectra of (I), decoupled (bottom) and coupled (top).

Figure 4.  $^{13}$C NMR spectra of (II), decoupled (bottom) and coupled (top).

Figure 5.  IR spectra of (I) (bottom) and its polymer (top) (KBr pellet).

Figure 6.  Mass-spectral decomposition of (I) and (II).

Figure 7.  TGA curve of (I) and (II) in nitrogen atmosphere at heating rate of $10^{\circ}$C/min.

Figure 8.  TGA curve of polymers, from (I) and (II) polymerized at $500^{\circ}$C for two hr, at heating rate of $10^{\circ}$C/min in nitrogen atmosphere.

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