AD-A130 580 SYNTHESIS AND SPECTRAL STUDY OF LOW DIMENSIONAL POLY-YNE POLYMERS CONTAIN..(U) BROWN UNIV PROVIDENCE RI DEPT OF CHEMISTRY I W SHIM ET AL. 13 JUN 83 TR-83-05 1/1

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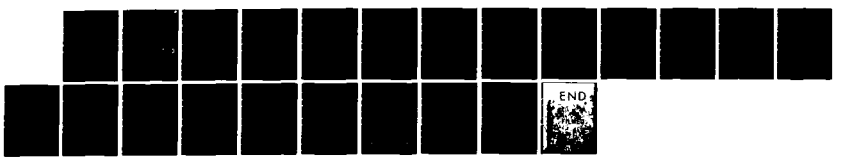

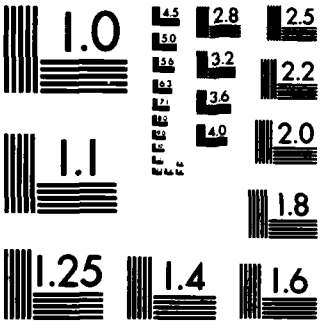

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A pseudo-one-dimensional poly-yne polymer (I) in which phthalocyanine silicon (PcSi) moities are bridged by p-diethynyl benzo groups has been obtained by salt elimination reaction from dichloro phthalocyaninato silicon and the disodium salt of p-diethynyl benzene in tetrahydrofuran (THF) solution. A soluble mixture of short chain oligomers of this polymer was also obtained. For parallel study, an analogous low dimensional poly-yne polymer(III) was synthesized by reaction of dimethyl dichloro silicon with disodium salt of diethynyl benzene in ether solution. Materials (I) and (III) were found to be stable in air and have good thermal stability. These two polymers were characterized by spectral and analytical data.

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Synthesis and Spectral Study of Low Dimensional Poly-yne Polymers Containing Phthalocyanine Silicon and Dimethyl Silicon in the Polymer Backbone

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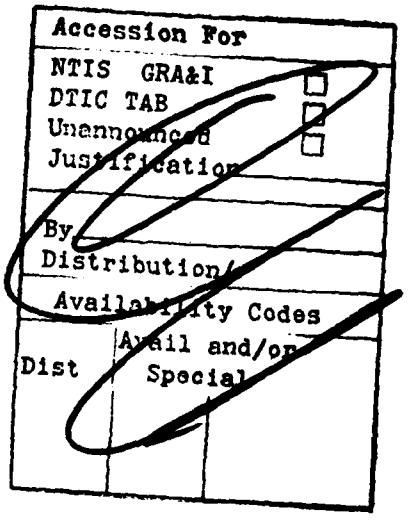

SUMMARY

A pseudo-one-dimensional poly-yne polymer (I) in which phthalocyanine silicon (PcSi) moieties are bridged by p-diethynyl benzo groups has been obtained by a salt elimination reaction from dichloro phthalocyaninato silicon and the disodium salt of p-diethynyl benzene in tetrahydrofuran(THF) solution. A soluble mixture of short chain oligomers of this polymer was also obtained. For parallel study, an analogous low dimensional poly-yne polymer(III) was synthesized by reaction of dimethyl dichloro silicon with disodium salt of diethynyl benzene in ether solution. Materials (I) and (III) were found to be stable in air and have good thermal stability. These two polymers were characterized by spectral and analytical data.

Introduction

One-dimensional organometallic polymers have received much attention recently because of their potential for having interesting optical and electronic properties, especially high electrical conductivity, and because they could exhibit interesting catalytic activity. In 1981, Hanack et al (1) proposed a conceptual model for a new kind of one-dimensional conducting material which would include macrocycles such as phthalocyaninate (Pc^{2-}) or hemiporphyrazinate(Hp^{2-}), a quadrivalent metal like Si, Ge, Sn, and a linearly bridging bidentate species like C_2^{2-}, as shown in Figure 1a. They suggested that this polymeric backbone structure with a face-to-face stacked macrocycle arrangement might give rise to efficient electronic charge transport. We note, in addition, that the macrocyclic moiety has important visible light absorption properties that it can impart to a polymer in which it is incorporated.

In 1982, Takahashi et al (2) reported that a type of poly-yne polymer containing a transition metal and a conjugated acetylenic bridging unit could be obtained by polycondensation reactions. Thus, they obtained materials postulated as $[PD(C_2C_6R_4C_2)]_n$, where PD and R represent the $Pd(PBu_3)_2$ moiety and alkyl groups respectively, by reaction (1).

$$t\text{-}PDCl_2 + HC{\equiv}C\text{-}C_6R_4C{\equiv}CH \xrightarrow[CuI]{PBu_3,\ HNEt_2} [PD\text{-}C{\equiv}C\text{-}C_6R_4\text{-}C{\equiv}C]_n \qquad (1)$$

R: H, CH_3, CH_3CH_2.

PD: $Pd(PBu_3)_2$

They found that p-diethynyl benzene can function as a good linear bridging reagent under the proper conditions.

In order to realize a compound of the type shown in Figure 1a, we have taken advantage of the ability of the ($-C\equiv C-C_6H_4-C\equiv C-$) moiety of p-diethynyl benzene to function as a linear bridge. We report the synthesis and characterization of the one-dimensional polymer (I), containing phthalocyanine silicon with a p-diethynyl benzene as a bridging unit, by reaction (2). In place of a polycondensation reaction which does not proceed for these compounds, reaction (2) was designed and occurs as a salt-elimination in which $PcSiCl_2$ combines with the disodium salt of p-diethynyl benzene (DSS). Two products are obtained in addition

$$PcSiCl_2 + NaC\equiv C-C_6H_4-C\equiv CNa \xrightarrow[(2)\ H_2O]{(1)\ \text{reflux in THF}} [PcSi-C\equiv C-C_6H_4-C\equiv C]_n \qquad (2)$$

to NaCl. One is an insoluble polymer (I) and a THF soluble polymer (II). In reaction (2), Pc is the phthalocyanine ring, $(C_8H_4N_2)_4$.

To develop the reaction chemistry and to assist in the interpretation of the spectral data on the principal product, the analogous reaction (3) of $(CH_3)_2SiCl_2$ with DSS was also carried out.

$$(CH_3)_2SiCl_2 + NaC\equiv C-C_6H_4-C\equiv CNa \xrightarrow[(2)\ H_2O]{(1)\ \text{ether}} [(CH_3)_2Si-C\equiv C-C_6H_4-C\equiv C]_n \qquad (3)$$

This results in product (III), also polymeric, in addition to NaCl.

Results and Discussion

The new materials synthesized, polymers (I), (II), and (III), are thermally stable and inert to air. Only product (II), a mixture of oligomers related to polymer (I), is soluble in various organic solvents and it has an average molecular weight of 1683±100.

The synthetic route employed to make these low dimensional polymers was based on salt elimination during the reaction of dichlorosilicon compounds with organometallic compounds such as the lithium, sodium, or magnesium derivatives of a bridging reagent. Although this approach is straightforward in principle, in preliminary work, experimental difficulties were encountered in making pure dimetal salt, or di-Grignard reagents of p-diethynyl benzene,

$$HC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CH + 2BuLi \xrightarrow{ether} LiC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CLi \qquad (4)$$

$$HC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CH + 2\ RMgBr \xrightarrow{ether} BrMgC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CMgBr \qquad (5)$$

because the exact stiochiometric amount of n-BuLi, or RMgBr must be used. Otherwise, either disproportionation occurs to yield monometallic derivatives (reaction (6))

$$XC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CX + HC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CH \longrightarrow 2XC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CH \qquad (6)$$

X: Li, MgBr

or unreacted n-BuLi, or RMgBr remains and can act as a terminator during polymerization. In the case of sodium, however, it proved possible to make the pure dimetallic salt of diethynyl benzene and avoid these problems.

Attempts to prepare these materials by polymerization of $PcSiCl_2$ and p-diethynyl benzene through a polycondensation reaction, using catalytic amounts of CuI and excess diphenyl amine under reflux conditions, were unsuccessful.

The typical infrared spectral data for the polymers and p-diethynyl benzene are summarized in Table 1, and the spectra of p-diethynyl benzene, $PcSiCl_2$ polymer (I), (III), and the brominated polymer (III) are given in Figures 2 and 4.

A. Polymers (I) and(II) from the reaction of $PcSiCl_2$ and DSS.

The pseudo linear one-dimensional structure of the polymer (I), and the progress of the reaction can be deduced from the infrared spectra. The strong antisymmetric Si-Cl stretching band at 468 cm^{-1} for $PcSiCl_2$ disappears completely during the polymerization reaction. The infrared spectrum of polymer (I) shows a number of characteristic bands of the macrocyclic silicon unit at 1611, 1427, 1334, 1290, 1165, 1123, 1081, 911, 760, 731, 575, 530 and 430(cm^{-1}). In addition, there are several bands which originate from the bridging unit ($-C\equiv C-C_6H_4C\equiv C-$) and terminal unit ($-C\equiv C-C_6H_4C\equiv C-H$) of the polymer backbone at 3290 (acetylenic C-H stretching), 2194 (bridging triple bond stretching), 2108 (terminal triple bond stretching), 1518, 1506, 1220, 1019 (carbon-carbon double or single bond stretching), 837 (C-H bending of benzene), and 648, 619cm^{-1} (acetylenic C-H bending). (See Figures 1b and 2.)

For the THF soluble polymer (II), all of the infrared bands except those on the 2100-2200 cm^{-1} region are seen at the same positions, but with relatively weaker intensity, when compared to those of polymer (I).

In the carbon-carbon triple bond stretching region, there are two bands at 2135 and 2108 cm^{-1}, which can be assigned to bridging and terminal triple bond stretching, respectively. Considering that polymer (II) has a short average

chain length (M.W., 1683), the bond at 2135 cm^{-1} is believed to come from the bridging carbon-carbon triple bond of short chain polymer backbone, and the band at 2194 cm^{-1} of polymer (I) from that of longer polymer backbone (see Figure 3). The increase in triple bond stretching frequencies from 2108 cm^{-1} to 2134 cm^{-1} to 2194 cm^{-1} is assumed to be related to the stronger interaction between the empty 3d orbitals of silicon atom and the conjugated π-orbitals of diethynyl benzene bridging unit.

As to the acetylenic carbon-silicon stretching assignment, there are only a few related reports. In 1979, Nakovich, et al, reported the infrared spectral study of 1,4 bis (trimethyl silicon), 1,3 buta-diyne, in which a band at 557 cm^{-1} could be assigned to acetylenic carbon silicon stretching band (4). In the case of polymer (I) and (II), there is a new band at 554 cm^{-1} and this band is assigned to the corresponding acetylenic carbon-silicon stretching mode.

Since it would be interesting to know the chain length (molecular weight) of the insoluble polymer (I), it is tempting to estimate it from infrared band intensity ratios despite the realization that absolute absorptivities per vibrating unit are not known. However, if the absorptivity of the 911 cm^{-1} band, which is due to an internal Pc mode, is the same in (I) and (II), and that of the 2108 cm^{-1} band due to terminal carbon-carbon triple bond vibration is the same for the two products, an estimate can be made since the molecular weight of each product is a unique function of the ratio of Pc to terminal carbon-carbon triple bond groups. Making these assumptions and using the ratio of the ratio of absorptivities of these two bands in the infrared spectra of (I) and (II), we estimate the molecular weight of polymer (I) to be about $6x10^3$, suggesting the presence of an average of 9 repeat units.

Bromination of polymer (I) in ether solution occurred as a simple addition of bromine to carbon-carbon triple bonds. In the infrared spectrum, all of the

bands that are related to the triple bond, such as 3290, 2194, 2108, 650, 617, 554 (cm^{-1}) disappear and a new band at 1680 cm^{-1} appears. It is characteristic of a carbon-carbon double bond stretching mode.

In the visible-ultraviolet absorption spectra, there are two significant changes upon polymerization. First, one of the two characteristic strong bands (670, 742 nm) of phthalocyanine ring in the visible region is shifted from 670 nm to 648 nm. It is assumed that there is some interaction between the diethynyl benzene bridging unit and the macrocycle ring system like charge transfer since there was no appreciable change in the visible spectrum when the trans-bis-axial chlorides of $PcSiCl_2$ were substituted by two lithium phenyl acetylides (1). The 742 nm band, however, is unshifted. Second, after the polymerization reaction there is an intense new absorption band at 368 nm, which is of the type expected for highly conjugated polymer systems. The strong electronic absorption bands in the 340 - 400 nm region have been observed in transition metal poly-yne polymers (2,5-8) and poly (xylylidene)s (9). The uv-vis features of (I) and those of $PcSiCl_2$ and p-diethynyl benzene are listed in Table 2.

B. Polymer (III) from the reaction of $(CH_3)_2SiCl_2$ and DSS.

In a 1966 patent disclosure (10), the General Electric Co. reported an analogous light yellow polymer produced by the reaction of $(Et)_2SiCl_2$ and the dilithium salt of diethynyl benzene in ether solution followed by an oxidative coupling reaction, but no spectral data were reported. Our polymer (III) is formulated as $[(CH_3)_2Si-C\equiv C-C_6H_4C\equiv C-]_n$ and is assumed to have a zig-zag type structure, resulting from the retention of tetrahedral geometry around sp^3 hybridized silicon atom.

In the infrared spectrum of polymer (III), there is a strong band at 2159 cm^{-1} and weak one at 2108 cm^{-1} which correspond to bridging and terminal

carbon-carbon triple bond stretching modes, respectively. The band at 2159 cm^{-1} is very close to the bridged carbon-carbon triple bond stretching frequency (2158 cm^{-1}) of the related $P\text{-}C_6H_4(C{\equiv}C\text{-}SiMe_3)_2$ compound (11). (See Fig. 4).

In addition to these, there are several infrared bands which belong to the bridging and the terminal diethynyl benzene units at 3300, 1915, 1601, 1504, 1407, 1223, 1159, 1105, 1020, 839, 665, 646, and 618 cm^{-1}. And the characteristic bands of the $(CH_3)_2Si$ moiety, namely $Si\text{-}CH_3$ bending and wagging bonds, appear at 1253 and 788 cm^{-1}. In the infrared spectrum of polymer (III) taken in a KBr disk, the C-H stretching band of methyl groups was observed at 2960 cm^{-1} and that of 1,4 disubstituted benzene was found at 3025 cm^{-1}, as would be expected. As in the case of polymer (I), a new band at 557 cm^{-1} appears and is assigned to the acetylenic carbon-silicon stretching bond. This band at 557 cm^{-1} disappeared after bromination of polymer (III), as did all of the triple bond related bands (3300, 2159, 2108, 646, 618 cm^{-1}), while a new band appeared at 1705 cm^{-1} due to the resulting carbon-carbon double bond stretching mode. There was no evidence of breakage of the polymer backbone during the bromination reaction.

The conductivities of compressed pellets of products (I) and (III) and of brominated (I) were found to be less than $1x10^{-8}$ $\Omega^{-1}cm^{-1}$.

Finally, we can conclude that the pseudo-one-dimensional polymer (I) as well as the low dimensional polymer (III) have been synthesized by salt elimination. Bromination of polymers (I) and (III) in ether solution under the conditions specified does not lead to ring-level interaction, but leads to simple addition of bromine to the carbon-carbon triple bonds and results in the formation of the brominated double bonds. The newly synthesized polymers (I) and (III) are thermally stable, inert in air, and have been characterized by spectral and analytical data.

Experimental

All reactions were carried out in an atmosphere of dry nitrogen and all solvents were carefully dried and deoxygenated. The dichlorophthalocyaninato silicon ($PcSiCl_2$), and dimethyl dichlorosilicon [$(CH_3)_2SiCl_2$] obtained from Alfa Inorganics, and purified before reaction by washing with acetone, and distillation respectively.

The infrared spectra were measured on a Digilab FTS-15B Spectrometer and ultraviolet- visible absorption spectra were measured on a Perkin-Elmer 552A Spectrometer. Elemental analyses and the molecular weight measurement were conducted by the Galbraith Lab. Inc. and Schwartzkopf Microanalytical Laboratory.

The p-diethynyl benzene was prepared as reported (3) and was identified by its infrared, and nmr spectra and its melting point (95°C).

Preparation of the disodium salt of p-diethynyl benzene (DSS).

This salt was prepared by the reaction of p-diethynyl benzene (5.04 g, 40 mmole) and sodium metal (1.84 g, 80 mmole) in dry ether solution (50 ml) under dry N_2. In a typical reaction, a mixture in these amounts was stirred for 48 hr at room temperature in a 250 ml round bottom flask. The evolved H_2 gas was released frequently through the vacuum line. The dark grey DDS was filtered and washed with ether. To confirm that no terminal protons remained unreacted, a sample of the DDS product was deuterated by dissolving it in D_2O and its ^1H-nmr spectrum was taken. In the nmr spectrum derived from each DSS sample used, no trace of unreacted terminal protons of p-diethynyl benzene, which would give a singlet at δ=3.19 ppm, was found.

The polymerization reaction of $PcSiCl_2$ and DSS.

In typical reaction 3 g of $PcSiCl_2$ (4.90 mmole) was added slowly to 60 ml

of a THF solution of DSS (2.5 g, 14.70 mmole). The mixture was refluxed for 7 days and then the THF was removed under reduced pressure. To destroy unreacted excess DSS and to remove NaCl, water was added dropwise to the solid and removed by filtration. The NaCl produced was identified by the reaction with $AgNO_3$ and the formation of AgCl. The dark greenish blue polymer product was washed with ether and THF several times. The insoluble polymer product (I) was filtered and dried at 110°C in vacuum. (Yield, 85% by weight). Anal. Calcd for $[PcSiC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}C]_n$: $C_{42}H_{20}N_8Si$; C, 75.89%; H, 3.03%; Si, 4.22%. Found: C, 75.31%; H, 3.95%; Si, 4.32%. The THF-soluble polymer (II) was collected in 9% yield by evaporating the THF solution from the filtrate in above washing procedure and by washing it with ethanol to remove p-diethynyl benzene. The measured molecular weight of the THF-soluble polymers (II) was 1683 (thermo-electric measurement by osmometry), which is the average for the soluble molecules. Both polymer product (I) and (II) were found to be stable in air until 320°C and seem to be quite thermally stable at higher temperature.

Polymerization reaction of $(CH_3)_2SiCl_2$ and DDS.

Freshly distilled $(CH_3)_2SiCl_2$ (2 g, 15.50 mmole) was added slowly by syringe to an ether solution (50 ml) of DSS (7.91 g, 46.54 mmole) in a 250 ml round bottom flask, and stirred for 4 days at room temperature. After reaction, the mixture was filtered under dry N_2 and ether (20 ml) was added again. Then water was added dropwise to the resulting ether solution and removed by filtration. This pale yellow polymer product (III) was washed with water and ether, and dried at 100°C in vacuum (yield, 97% by weight). Anal. Calcd for $[(CH_3)_2Si\text{-}C{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}C]_n$: $C_{12}H_{10}Si$; C, 79.06%; H, 5.53%; Si, 15.41%. Found: C, 78.86%; H, 5.93%; Si, 15.19%. This polymer III was stable in air and decomposed at 220°C.

Bromination of polymers (I) and (III).

Bromine was added dropwise to ether solutions of each polymer at room temperature until the bromine color persisted and the resulting solutions were stirred for 4 hrs. After reaction, the solvent was evaporated under reduced pressure. The resulting residue was washed with excess ether and dried at 100°C in vacuum.

Acknowledgment

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Table 1

IR Spectral* Data in Nujol Mull (cm^{-1})

Compounds	ν(≡C-H)	ν(C≡C)	ν(C≡CH)	**δ(Ph-H)	ν(Si-C≡)	ν(⊐C=C⊏)
HC≡C-C_6H_4-C≡CH	3268(S)	·	2105(W)	837(S)	·	·
	3310(S)		2115(W)			
Polymers						
I	3290(W)	2194(W)	2108(W)	838(S)	554(W)	·
II	3290(W)	2135(W)	2108(W)	838(M)	554(W)	·
III	3300(W)	2159(S)	2108(W)	841(S)	557(M)	·
Brominated polymers						
I	-	-	-	838(M)	-	1680(M)
III	-	-	-	842(M)	-	1705(M)

* Relative intensities: S, strong; M, medium; W, weak.

** Characteristic C-H bending mode of 1,4 disubstituted benzene

Table 2

UV/VIS spectral data in nujol mull

Compounds	λ max.(nm)
$HC{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CH$	208, 214, 258, 271, 291
$PcSiCl_2$	229, 276, 388, 670, 742
Polymer (I)	207, 289, 368, 388(sh), 648, 742

Figure Captions

Figure 1. Psuedo-one-dimensional polymers:

(a) conceptional model suggested for synthesis by M. Hanack, et al (1),

(b) the supposed structure of polymer product (I) in this work, where M is silicon.

Figure 2. Infrared spectra of A) p-diethynyl benzene, B) $PcSiCl_2$, and C) polymer (I) in nujol mull.

Figure 3. Infrared spectra in 2100-2200 cm^{-1} region a) p-diethynyl benzene, b) polymer (II), and c) polymer (I).

Figure 4. Infrared spectra of A) polymer (III), and B) brominated polymer (III).

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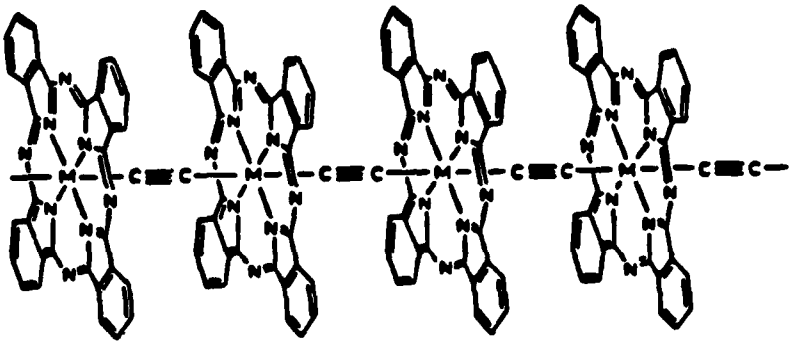

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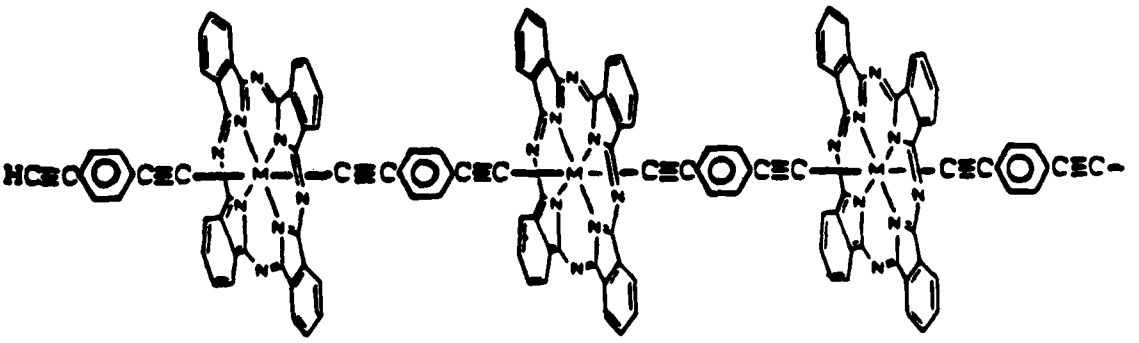

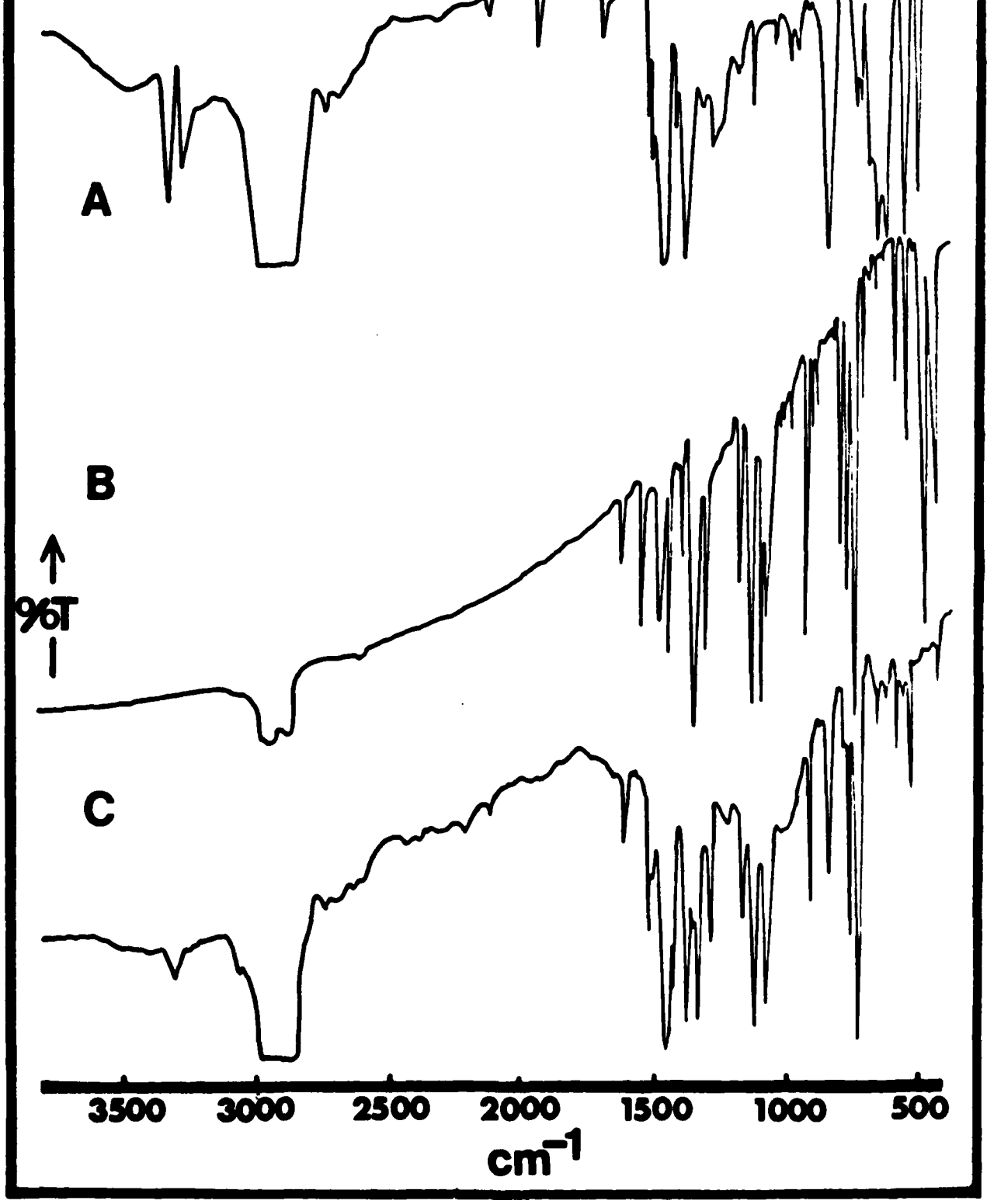
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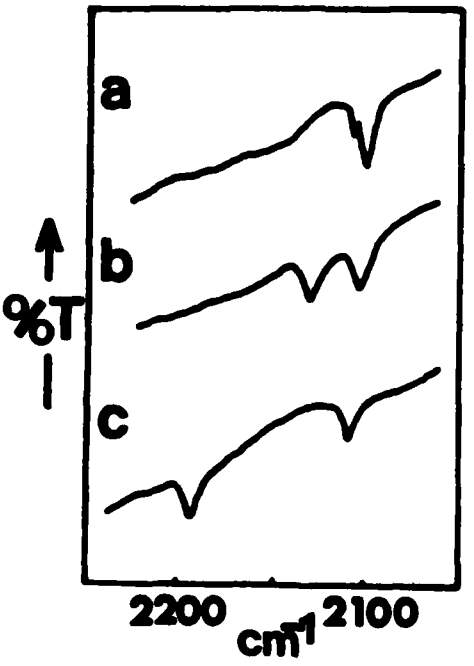
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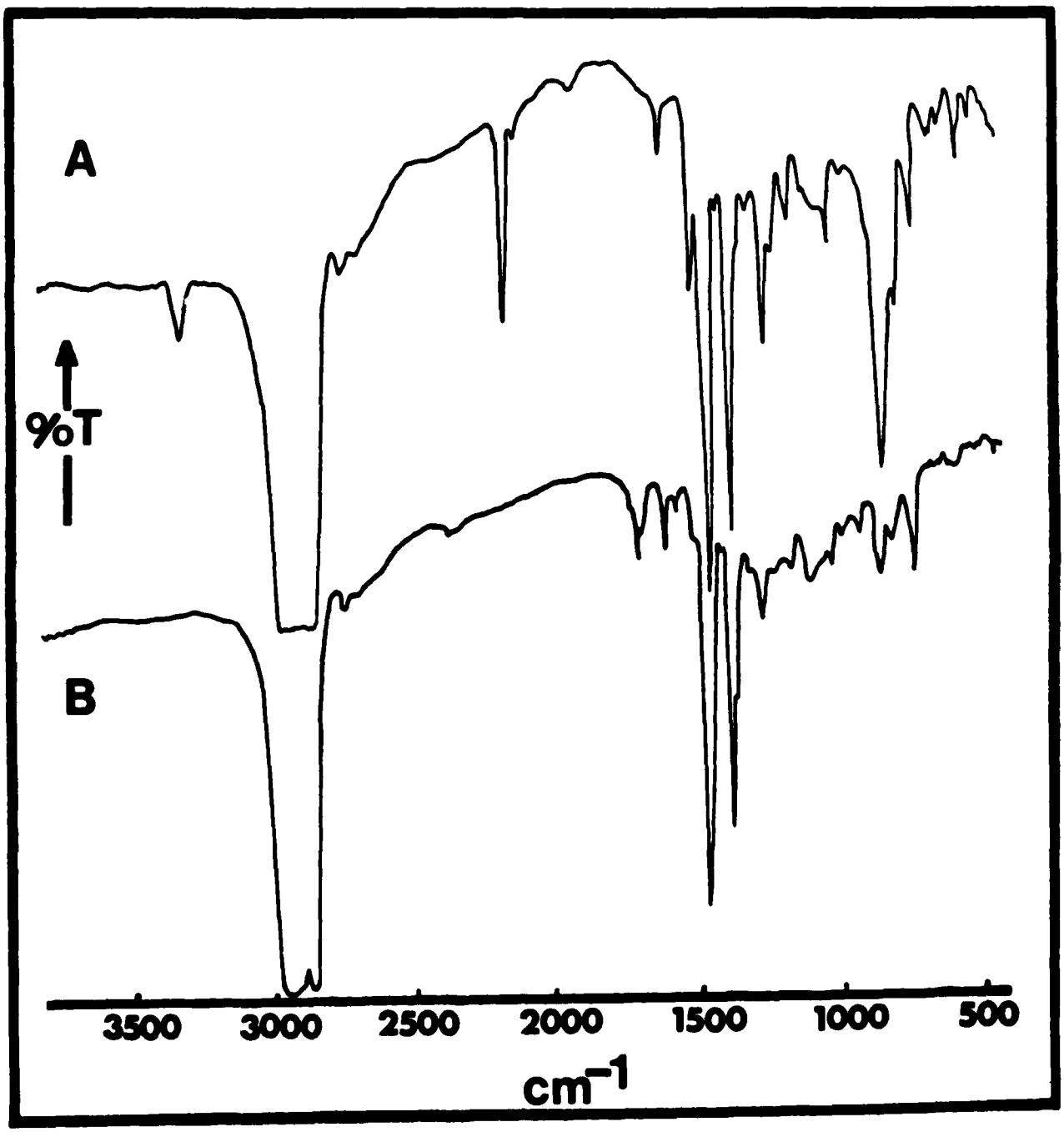
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