SPROUSE COLLECTION OF INFRARED SPECTRA

BOOK I: POLYMERS

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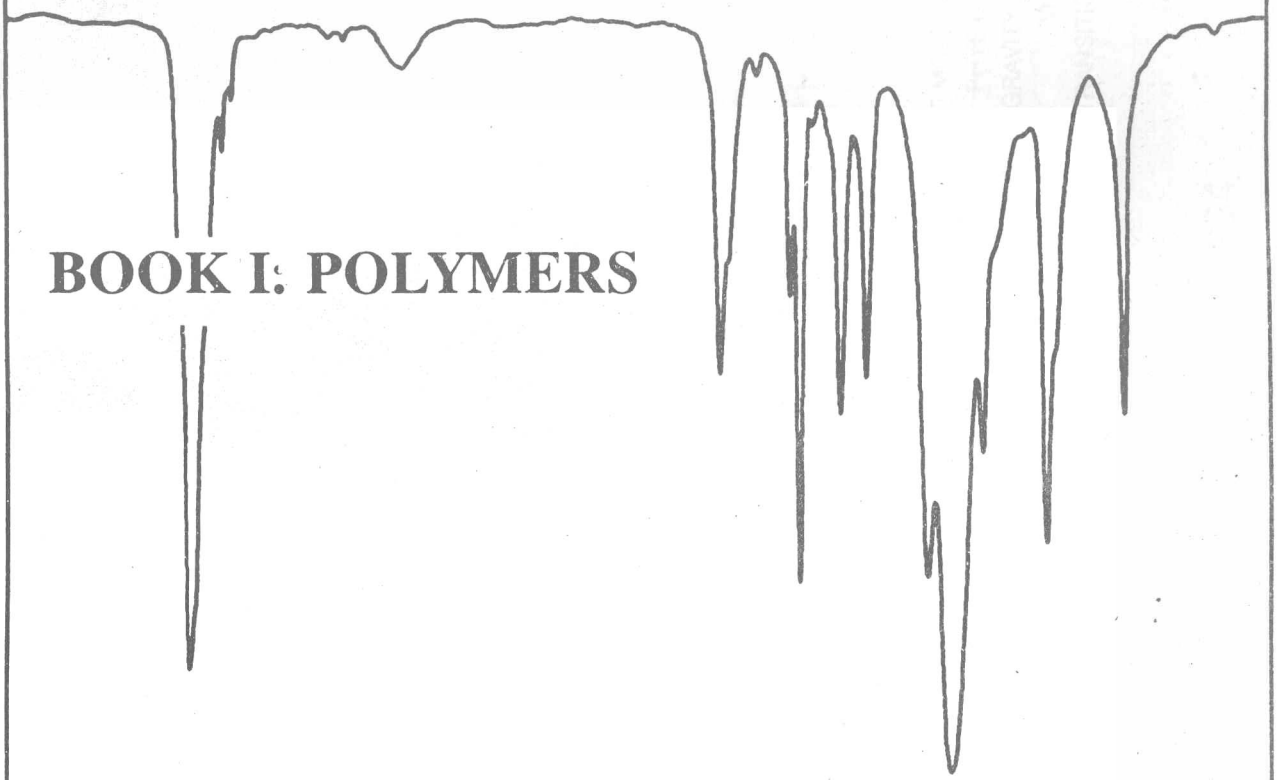

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BOOK I: POLYMERS

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PREFACE

SPROUSE COLLECTION OF INFRARED SPECTRA, BOOK I:POLYMERS is the first in a series of reference spectra collections to be published by Sprouse Scientific Systems over the next few years. The objective of these collections is to provide reliable, high quality reference spectra that can be used for structural elucidation, qualitative analysis, quantitative analytical methods development, computerized library searching, and software and algorithm development. The spectra are measured on state-of-the-art Fourier Transform Infrared (FTIR) Spectrometers. Thus they provide the technical community with a source of reference spectra, in both printed and digital formats, that are on the same technological level as the FTIR hardware that is being used in today's laboratories.

During the last decade, the evolution of computerized infrared spectrometers has placed more stringent demands on reference data. Spectra of mediocre quality no longer stand up to today's demands. Applications software allows the user to check frequency calibration, band absorption adherence to the Beer-Lambert law, and to isolate contaminant bands easily. Reviewing and comparing large numbers of reference spectra, either for unknown identification or data quality control, is facilitated by the availability of computer software. The use of technological advancements in laboratory instrumentation and computerized spectral manipulation software is reflected in the quality of reference spectra published in recent handbooks such as Instrumental Data for Drug Analysis, by the Georgia Bureau of Investigation, and The Aldrich Library of FTIR Spectra. These books, as well as our SPROUSE COLLECTION OF INFRARED SPECTRA, reflect the efforts being made to raise the quality of reference spectra available to the technical community to meet current day standards and needs.

The polymer reference spectra compiled in this book represent nearly all of the principle component polymeric materials in common use today. Although there are many different commercial formulations using these materials, or proprietary modifications of them, there are not a large number of different polymeric base materials in common usage. In this collection, we have compiled reference spectra for 415 samples grouped into 15 chemical classes. Of these, we were able to draw representative molecular structures for 392 of the materials. Only 215 of the materials possessed a unique molecular structure after excluding the various homopolymers, copolymers and terpolymers which varied only in chain length, molecular weight range, or oligomeric ratios.

A considerable effort was made to identify each material by chemical name and to draw its general molecular structure. Tradenames and acronyms are presented as alternate names and are used only as support information. We have also provided an alphabetical index that allows the user to locate reference spectra based on any polymer constituent within a material. Therefore, materials containing more than one polymeric constituent, copolymers, terpolymers, etc. have been listed in the alphabetical index under the chemical name for each component. Additionally, each spectrum has been listed under its primary chemical name, and under each synonym.

Finally, we have attempted to produce this collection of infrared spectra with a minimum number of errors. The latest developments in infrared spectroscopy, computer hardware and software have been used to ensure the highest quality reference spectra. We have used both our own and commercially purchased software tools to satisfy our particular spectroscopic data processing and quality control needs. Each hard copy spectrum published in this collection was plotted from its digital spectrum; therefore, we are able to provide the reference spectra in both digital and book format. The true quality of the reference spectra, however, lies in how accurately the spectra reflect the chemical compounds from which they were measured. The authenication process still remains the largest task in producing a reference collection of spectra. Each spectrum must be reviewed several times along with the sample molecular structure in order to insure its accuracy. Our personnel have thoroughly reviewed the spectra in this collection. Numerous replacement samples were obtained to remeasure spectra when contaminate bands were found during the review process. In any task where a large amount of technical information is accumulated, errors are never totally eliminated. However, we believe the errors have been minimized. We solicit your comments and suggestions on this book in order to improve upon the new collections to follow in the series. Our goal is to provide infrared spectroscopists with extremely high quality reference data in a format which is useful and easy to use.

James F. Sprouse, Ph.D.
President
Sprouse Scientific Systems, Inc.

INTRODUCTION

HANDBOOK ORGANIZATION

The spectra in this handbook are arranged by chemical class and in order of increasing structural complexity. The book begins with the straight chain aliphatic hydrocarbons, e.g. paraffin, and finishes with the very complex polysaccharides. Within each chemical class, the corresponding halogenated polymers are included, listed in increasing amount of substitution. Copolymers, terpolymers and other compounded monomers are generally categorized under the chemical class of the major polymeric constituent. However, the alphabetical index allows the reader to easily locate copolymers and terpolymers by any of the homopolymer groups. If the major component is known, then that grouping should be initialllly searched. At the beginning of each chemical class is a general information page. This page gives the user general technical information pertaining to the polymers that it precedes. At the top of the page is a brief description of the chemical class including polymer synthesis, useful processing information and general applications of the polymers. General definitions of the technical terms used throughout the general information pages are located on page viii. Following the product information are general transmission spectra which are representative of the polymers within that classification. The spectra allow the user to become familiar with the major band representations of the class. Superimposed on the spectra are the wavenumber locations of the major bands and the structural assignments they represent. A general solubility chart is also located on the information page. This gives the user a quick reference to the common solvents and non-solvents of the major polymers within that chemical class. Three indices are included in this handbook. These include: (1) a numerical index, listed by increasing spectrum number. This number is located at the center top or bottom of each page for each spectrum in the book. (2) an alphabetical index, including several common manufacturer tradenames and many chemical synonyms and acronyms, and (3) a Chemical Abstracts Service registry number index.

TECHNICAL INFORMATION

The majority of samples used to compile this collection of reference spectra were supplied by Scientific Polymer Products,Inc. (SP^2), 6265 Dean Parkway, Ontario, New York, 14519. For the convenience of the user, the SP^2 catalog number is presented as part of the technical information provided with the spectra. For polymer samples obtained directly from commercial manufacturers, the company name and sample tradename are given as part of the technical information. All data is given in degrees Celsius unless otherwise stated. Abbreviations given throughout the book are defined on page ix.

SAMPLE PREPARATION

Polymer samples were received from suppliers as solids, liquids and solutions. The solid samples were dissolved in an appropiate solvent and a thin film was cast onto potassium bromide (KBr) salt plates. Liquid organic samples were measured neat between two KBr salt

plates and the aqueous samples between two silver chloride (AgCl) plates. Polymers obtained in solution were prepared as films and cast directly onto KBr salt plates (or AgCl for aqueous solutions) by evaporating off the solvent. In some cases, films were cast onto a stainless steel plate, then the film was transferred to salt plates for measurement of the spectrum. Extreme care was taken to avoid residual solvent band contamination in the polymer spectra. The following is an explanation of the abbreviations used in this book for sample preparation techniques:

Neat - A liquid sample was prepared as a thin film between two KBr salt plates.

Solvent/Cast - A solid sample was dissolved in an organic solvent. Then a film of the solute was cast onto a KBr plate by evaporating the solvent. The actual name of the solvent is given, e.g. Touene/Cast.

Melt - The sample was melted and spread into a film between two KBr salt plates. It was then allowed to recrystallize at room temperature before the spectrum was measured.

KBr - A hygroscopic sample was ground into a powder using a mortar and pestle and then pressed into a KBr matrix using 6.8 metric tons of pressure.

Film/AgCl - A liquid sample was prepared as a thin film between two AgCl salt plates.

H_2O/Film - A solid sample was dissolved in water. Then a thin film of the solute was cast onto a polished stainless steel surface and the solvent evaporated. The resulting polymer film was lifted and placed between two KBr salt plates for measurement of the spectrum.

H_2O/Cast/AgCl - A solid sample was dissolved in water. Then a thin film of the solute was cast directly onto an AgCl plate by evaporating the solvent.

INSTRUMENTATION

All reference spectra were measured on a Digilab Model FTS-40 Fourier Transform Infrared Spectrometer. All spectra were measured at a nominal resolution of 2 wavenumber (cm^{-1}) over the mid-IR spectral range of 4400-400 cm^{-1}. Data were collected with sufficient signal averaging to provide signal-to-noise ratio greater than 5,000 to 1 over the entire spectral region. Samples were carefully prepared in order to provide strongest band absorbance in the range between 0.5 and 1.5 absorbance units. Measurement time was typically 3 minutes, which corresponds to co-adding 64 spectra on the Digilab FTS-40. However, measurement time was adjusted based on sample thickness in order to achieve the desired signal-to-noise ratios.

QUALITY CONTROL

The infrared spectrometer was tested for frequency calibration, photometric accuracy and baseline stability on a routine basis throughout data measurement. In addition, all spectra

were very carefully checked for residual solvent bands and sample contamination. The following quality control methods were used:

1) Wavenumber Calibration

The IUPAC (International Union of Pure and Applied Chemistry) recommended wavenumber standard material was used for the spectrometer wavenumber calibration. Two mixtures were used:

a) A solution of 98.4 parts Indene, 0.8 parts Camphor and 0.8 parts Cyclohexanone (wt/wt) was used to calibrate the spectral range between 4400-600 cm^{-1}.

b) A solution containing equal parts (wt/wt) of Indene, Camphor and Cyclohexanone was used to calibrate the spectral range between 600-400 cm^{-1}.

Infrared spectra of the two calibration mixtures were obtained using a 0.25mm fixed path length liquid cell. The peak positions of 50 bands were located and confirmed to the IUPAC assigned band locations. This performance check was run approximatley every 30 days. Carbon dioxide reference bands were used for daily wavenumber calibration checks. Peak positions were measured at 2361.6 ± 0.2, 2336.6 ± 0.2 and 668.5 ± 0.2 cm^{-1}.

2) Instrument Performance and Stability

The performance and stability of the instrument was monitored on a daily basis by measuring the RMS noise in a 100%T baseline at selected frequencies across the spectral range. The 100%T line was measured each day by taking the ratio of one single beam spectrum to another. The 100% line was plotted between 98 and 102%T and the RMS noise level was calculated in the spectral regions of 3950-4050, 1950-2050, 950-1050 and 450-550 cm^{-1}. A baseline with a maximum of 2% RMS peak-to-peak noise within these regions was used as the criterion for acceptable performance for this instrument.

3) Atmospheric Contaminants

The presence of water vapor, carbon dioxide and hydrocarbons were strictly monitored during sample scanning. The optical head was purged continuously with $N_{2(g)}$ boiled off from liquid nitrogen in order to minimize background contamination. Repeated scanning of the background and sample were made for total compensation of these contaminants. For spectra measured as KBr pellets, spectra containing water absorption bands were not accepted if their intensity exceeded 2%T peak-to-peak. Some water vapor bands are evident in the spectra despite thorough purging of the optical head with dry nitrogen. However, these background bands are generally obvious and do not interfere with the important spectral bands in the sample.

GENERAL POLYMER DEFINITIONS

Polymer - a large molecule comprised of repeating structural units joined together by covalent bonds. (The term is derived from the Greek: poly-many, meros-part.)

Copolymer - A polymer which contains more than one type of structural unit.

Terpolymer - A polymer which contains three types of structural units.

Random copolymer - copolymer in which the individual monomers are located in an unordered fashion e.g., -a-b-b-a-b-a-a-a-a-b-b-a-

Alternating copolymer - copolymer in which the individual monomers appear in alternating positions e.g., -a-b-a-b-a-b-a-b-

Block copolymer - copolymer in which the individual monomers are arranged in blocks or groups e.g. -a-a-a-b-b-b-a-a-a-

Graft copolymer - copolymer in which one or more of the monomers is grafted onto the primary chain either through transfer, chemical or irradiation grafting.

Tactic polymer - polymeric structure in which carbon atoms and their side groups are regularly arranged along the polymer chain.

Isotactic - polymeric structure in which there is repetition of the same configuration at each progressive asymmetric carbon atom along the polymer chain.

Syndiotactic - polymeric structure in which there is alteration in configuration at each progressive asymmetric carbon atom along the polymer chain.

Atactic polymer - polymeric structure in which the carbon atoms and their side groups are randomly arranged along the chain.

Thermoplastic - polymers which may be repeatedly heated, re-shaped and cooled without thermal decomposition.

Thermoset - infusible polymer in which the molecular chains are joined together by covalent bonds thus, not allowing the chains to slide past one another upon the application of heat and pressure (unless degradaion occurs).

Elastomer - as defined by ASTM, a polymeric material which at room temperature can be stretched to at least twice the original length and, upon immediate release of the stress, will return quickly to approximately its original length.

Bulk polymerization - method of polymerization involving a system composed totally of monomer/polymer and merely involves heating the mixture, resulting in a relatively pure polymer.

Solution polymerization - polymerization method in which the monomer is dissolved in a solvent prior to polymerization. This technique is primarily used in the ionic polymerization of gaseous vinyl monomers.

Suspension polymerization - polymerization method in which the monomer is dispersed in water in small droplets maintained by vigorous stirring. A monomer-soluble initiator is added and polymerization occurs within each droplet.

Emulsion polymerization - polymerization technique in which the monomer is dispersed in water containing a soap to form an emulsion. Polymerization is initiated within individual micelles.

TABLE OF ABBREVIATIONS

%-	weight percent unless otherwise specified
p -	specific gravity
d -	density
g/cm -	grams per centimeter (density)
n -	viscosity
cps -	centipoises (viscosity)
ctks -	centistokes (viscosity)
Tg -	glass transition temperature
Mooney visc -	viscosity measurement using Mooney viscometer
Ford #4 visc -	viscosity measurement using Ford viscometer (#4 spindle)
Brookfield -	viscosity measurement using Brookfield viscometer
MW -	molecular weight
Nom MW -	nominal molecular weight
Ave MW -	average molecular weight
Visc MW -	viscosity based molecular weight
Visc Avg MW -	viscosity based average molecular weight
Nom MN -	nominal number average molecular weight
EEW -	epoxide equivalent weight

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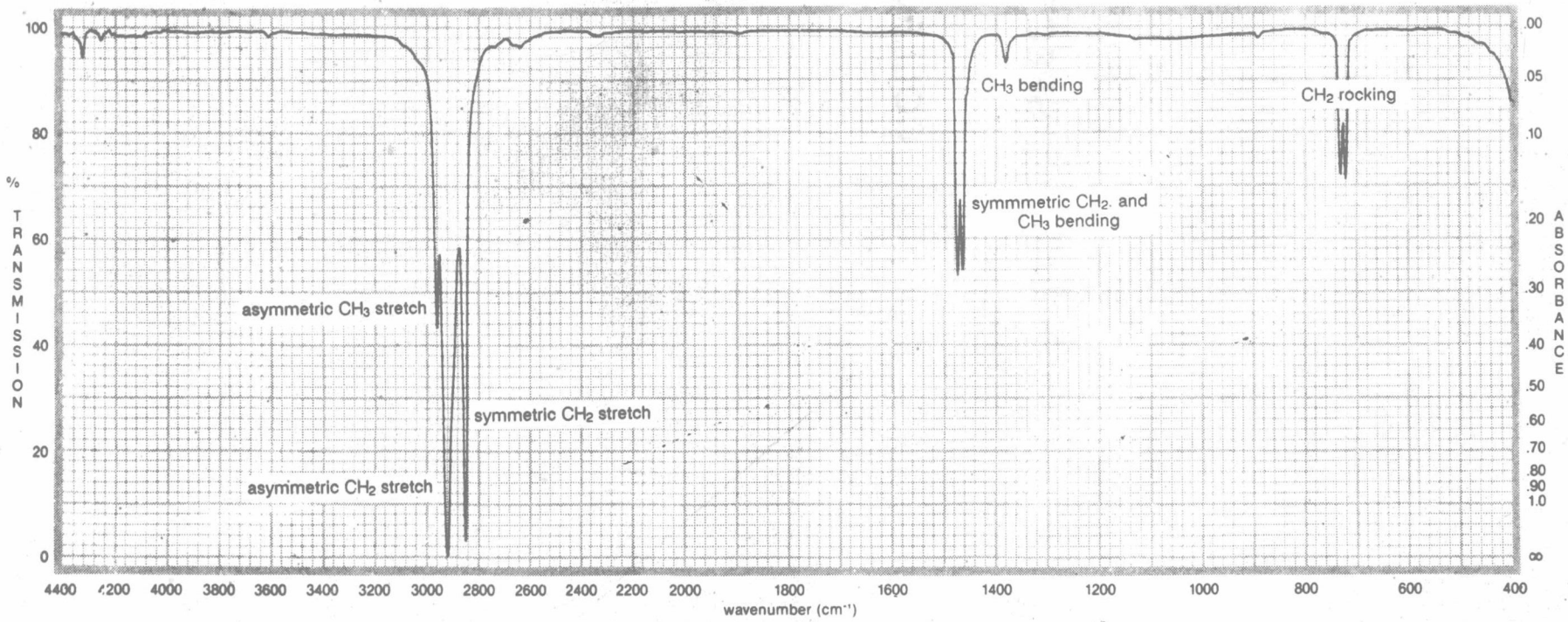
PARAFFINS

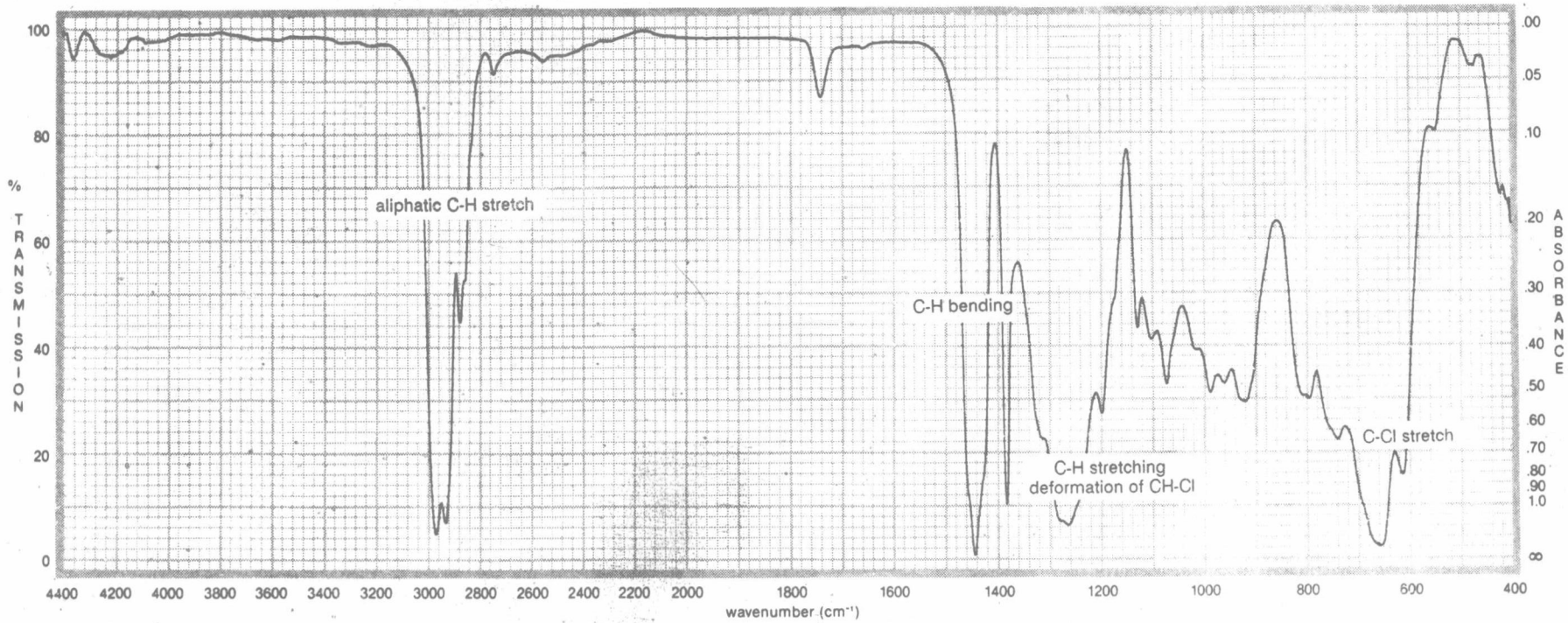
The general definition of a paraffin can be stated as a mixture of solid hydrocarbons (C17-C25) adhering to the general formula C_nH_{2n+2}. Paraffins exhibit a tendency to crystallize, becoming waxy at approximately C25. Although the primary natural source of paraffin is petroleum, it accounts for only 3-5% of petroleum's composition. The remainder consisits of lighter alkanes. To separate the paraffins, the oil is chilled and the wax is removed by filtration. Following purification, the wax is marketed as a commercial product, either in pure or chlorinated form.

APPLICATIONS: Paraffins are used for the manufacturing of wax paper and candles. They are used for waterproofing wood, cork, paper and leather, and are also found in lubricants, such as petroleum jelly.

PARAFFIN WAX



CHLOROPARAFFIN



POLYMER SOLUBILITY CHART

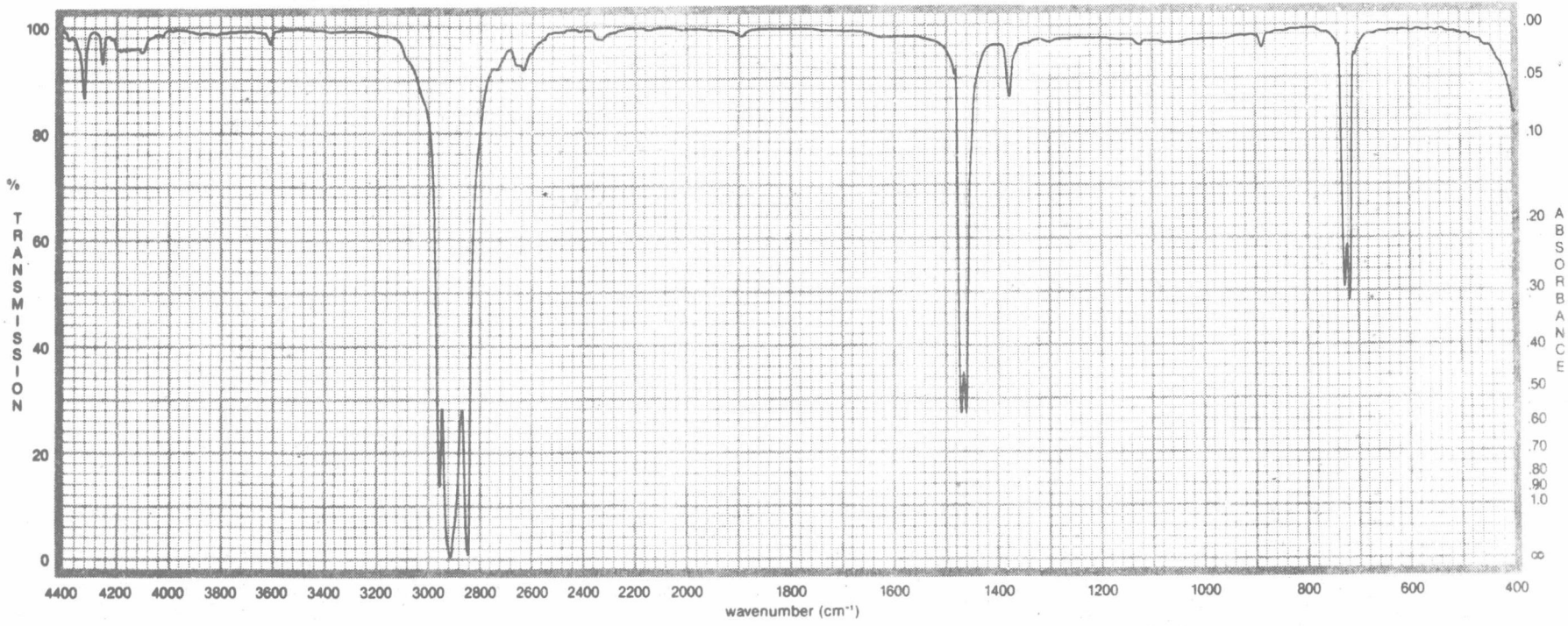
PARAFFINS	Chloroform	Xylene	THF	MEK	DMSO	DMF	Methanol	p-Dioxane	Acetone	H_2O
Paraffin	S	S	S	S	S	SS	SS	S	S	I
Chloroparaffin	S	S	S	S	S	SS	SS	S	S	I

S - Soluble ; SS - Slightly Soluble ; I - Insoluble

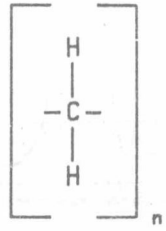
PARAFFIN WAX

SYNONYMS: PARVAN® 3150
HARD PARAFFIN
PETROLEUM WAX

CAS #: 64742-51-4
SOURCE: Exxon Company
SP2 #: –



TECHNIQUE: Melt



GENERAL FORMULA: $(C_1H_2)_n$

PHYSICAL PROPERTIES

MOLECULAR WT: –
PHYSICAL FORM: white, crystalline wax
SPECIFIC GRAVITY/DENSITY: 0.81/15.6
VISCOSITY: 3.7 cSt/98.9
GLASS TRANSITION TEMP: –