

FOURIER TRANSFORM INFRARED CHARACTERIZATION OF POLYMERS

Edited by Hatsuo Ishida

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Edited by
Hatsuo Ishida

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FOURIER TRANSFORM INFRARED CHARACTERIZATION OF POLYMERS



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PREFACE

This book contains the proceedings of the Symposium on FT-IR Characterization of Polymers, which was held under the auspices of the Division of Polymer Chemistry, American Chemical Society (ACS) during the annual ACS meeting in Philadelphia, August, 1984. The content of each paper has been substantially extended from the papers presented during the conference.

Due to the accidental, irrecoverable loss of the entire contents of the book by the computer system used for editorial purposes, the publication of this book has been delayed more than one year over the initial scheduled date. It has been a continuous, frustrating experience for the editor as well as for the authors. An extended Murphy's law, "anything can go wrong goes multiply wrong" has been demonstrated in editor's office. It necessitated, otherwise unnecessary, repeated proof reading during which time the editor had valuable experience in familiarizing himself with each paper much more than usual. The papers in this book are state-of-the-art even after such a delay. It is the authors pride and integrity toward the quality of each paper that makes the value of this book long lasting, while responsibility of the loss of any timeliness rests at the editor's hand. For the purpose of official records, submission and acceptance dates must be stated. All papers had been submitted by September, 1984, and had been accepted for publication by November, 1984, after the critical review processes.

Since the editor had seen the first FT-IR spectrum of a polymeric material, which was recorded by a modern computerized FT-IR spectrometer, little more than a decade ago, the application of FT-IR to the polymer science field has developed at an unprecedented rate in the history of IR spectroscopy. The first FT-IR related paper of the editor was initially rejected by a reviewer because the reviewer remarked, "I do not believe in FT-IR". Nowadays, some may be willing to go as far as saying, "The IR spectrum recorded by a dispersive instrument may not be

good enough". Some even propose that the use of the word "IR spectrum" should automatically indicate FT-IR spectrum. Advent of the table-top FT-IR spectrometers along with research grade spectrometers allow FT-IR to be used in all areas of industrial and academic IR studies. Of course, under any rapid growth, there is always a painful, persistent effort of the pioneers. We should thank researchers in pre-computerized FT-IR era for their valuable devotion. It is a fortuitous coincidence that the editor works at the university where Professor Michelson, the inventor of the Michelson interferometer which is the heart of FT-IR spectrometer, performed the infamous measurement of the speed of light using the interferometer exactly 100 years ago. It is also where the first paper on FT-IR characterization of polymers was written.

IR spectroscopy is one of the most valuable methods for polymer characterization. Unique sampling requirements arise from the polymeric nature of the samples. FT-IR has been extensively applied to polymers yet there has been no monographs dedicated to polymer characterization by FT-IR. The readers should enjoy a wide spectrum of articles in this book from the latest development of instrumentation to theoretical works utilizing the uniqueness of FT-IR.

The papers presented in the symposium have been rearranged in this book based on the content. Chapter I was later added to provide some background in optical theory. The contents of the remaining chapters are: Chapter II; Polarization-modulation Technique, Chapter III; New Instrumentation, Chapter IV; Application to Molecular Dynamics and Kinetics, Chapter V; Spectral Analysis and Manipulation Techniques, Chapter VI; Surface and Interface Studies, and Chapter VII; Application of Optical Theories.

It is the editor's privilege to acknowledge those who helped in editing this book. Each author's patience in spite of unacceptable delays was the major driving force for the progress. Ms. L. Piccinino and Ms. E. Raynor-Enco of Plenum Publishing Co. are both sponsoring editors who have been very patient and understanding with the delayed work. Ms. A. Lewandowski and Ms. P. Engelhorn helped to produce the book in its final form. The proof reading was done in part by R.T.Graf, J.D.Miller, H.Chatzi, R.Johnson, Y.Ishino, C.Scott, K.Nakata, K.Hoh, Y.Suzuki, J.Jang, and C.Khoo. Finally, wholehearted support from the editor's family members all made this book come to a completion.

H. Ishida
Editor

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INTRODUCTION TO OPTICS AND INFRARED SPECTROSCOPIC TECHNIQUES

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I. Polymer Infrared Spectroscopy

Infrared spectroscopy is one of the oldest techniques for the molecular level characterization of materials, and it has of course been extensively used to study polymer systems. Excellent review articles exist for the application of both dispersive [1] and Fourier transform instrumentation [2] to polymers. The use of IR to study polymer surfaces and interfaces has also been reviewed [3]. As the number and complexity of IR techniques for examining non-routine samples has increased, there has been a growing tendency to examine samples 'in situ'. This is especially true where polymer systems are involved. Infrared spectra of such systems as filled polymers, glass reinforced plastics, fibers, and surface treated particulates, have been recorded in the past using relatively old techniques such as transmission and ATR. However, the spectral quality was low. Now it is possible to obtain high quality spectra of these systems by using such techniques as diffuse reflectance, photoacoustic, and IR microscopy.

The emphasis on measuring samples 'as is' can lead to a dilemma in spectral interpretation. One may obtain a spectrum of an intractable sample by a suitable technique, but has one measured a spectrum of only the molecular structure of the sample, or a combination spectrum of the sample's molecular structure and macroscopic state? Furthermore does the technique itself contribute to the measured spectrum? For many samples, these questions may only be important for quantitative work. But, for other samples even qualitative IR spectroscopy is not feasible without an understanding of the underlying physics of the experiments. In an infrared experiment, one usually measures the transmission, reflection, emission, or scattering of IR radiation, and then calculates the absorption from the measured quantity.

Usually more than one of these phenomena is present for a given experiment, and one must either experimentally minimize the others or account for them by calculations.

II. Theory of Optics: Background

The classical description of the propagation of electromagnetic radiation in free space or matter can be derived from Maxwell's equations (*). This derivation involves solution of second-order differential equations for both the electric and magnetic fields. A variety of solutions to this differential equation are possible including spherical and plane wave. For problems involving the reflection and transmission of light at planar interfaces, the plane wave solution given below is a convenient format.

$$E = E_0 \exp(i\omega(n/c \cdot r \cdot s - t)) \quad (1)$$

n - refractive index c - speed of light
 r - position vector s - propagation vector
 E - electric vector $\omega = 2\pi\nu$ t - time

In this equation the electric field E is related to the initial electric field E_0 by a complex exponential term which contains the frequency and refractive index (**). In a transparent medium the refractive index n is real and the electric and magnetic fields travel without attenuation at a speed of c/n . In an absorbing medium the refractive index is a complex quantity and the wave is attenuated as it propagates. The complex refractive index can be written as:

$$\hat{n} = n + ik \quad (2)$$

where the real part n is referred to as the refractive index and the imaginary part k is referred to as the absorption index. Both quantities together are often called the optical constants or the complex refractive index. For an absorbing medium equation (1) can be rewritten as

(*) See references 4-6 for a complete description of classical electromagnetics and optics.

(**) Note that the the time dependence of the oscillating electric field is $-i\omega t$. It is also possible to have an $i\omega t$ time dependence.

(**) The refractive index is the square of the dielectric constant.

$$E = E_0 \exp(i\omega(n/c \, r.s - t)) \exp(-\omega/c \, k \, r.s) \quad (3)$$

where the second exponential term expresses the rate of attenuation as a function of the distance travelled ($r.s$). The intensity of the radiation is just the square of the electric field amplitude. The base 10 logarithm of the intensity gives Beer's Law.

$$I = E \cdot E^* = I_0 \exp(4 \pi k \, v \, d) \quad (4)$$

$$A = -\log_{10}(I/I_0) = 4 \pi k \, v \, d / 2.303 = ad \quad (5)$$

d - thickness a - specific absorptivity

The above equations apply to the propagation of electromagnetic radiation in a single homogeneous, isotropic medium. For any real experiment, multiple phases, and hence phase boundaries will be present. Figure 1 is a schematic diagram of the simple two phase, single interface situation. The angle of reflection equals the angle of incidence, and the angle of refraction is related to the incident angle by Snell's law:

$$(6) \quad n_1 \sin(\theta_1) = n_2 \sin(\theta_2)$$

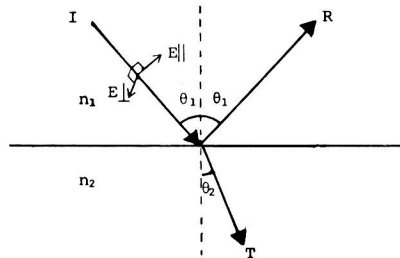


Figure 1. Schematic diagram of reflection and transmission at interface between two homogeneous and isotropic phases.

The fraction of the incident intensity (I) which is reflected (R) and transmitted (T) at a single interface can be calculated from the Fresnel relations. These equations are written in terms of the refractive indices of the two media, and the angle of incidence and refraction. There are four Fresnel relations for a

single interface: one for each polarization state for both the reflected and transmitted waves. The polarization of the electric field vector can be either parallel (p) or perpendicular (s) to the plane of incidence (see figure 1). The plane of incidence is defined as the plane containing the propagation vector and the surface normal vector. For figure 1 the plane of incidence is the plane of the page. For normal incidence, the plane of incidence is undefined and the Fresnel relations simplify to the following:

$$r = \frac{n_2 - n_1}{n_2 + n_1} \quad R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \quad (7)$$

r - Fresnel reflection coefficient

R - reflected intensity

$$t = \frac{2n_1}{n_2 + n_1} \quad T = (t)^2 (n_2/n_1) = \frac{4n_1 n_2}{(n_2 + n_1)^2} \quad (8)$$

t - Fresnel transmission coefficient

T - transmitted intensity

The Fresnel relations and Snell's law are also valid for absorbing media. In this case, since the refractive index is complex valued, the Fresnel coefficients also become complex.

The intensity of the reflected light as a function of the angle of incidence is plotted in figure 2 for two different interfaces. In this figure the first medium is a vacuum, and the second medium is either transparent (2A) or absorbing (2B). The refractive index of the dielectric is representative of ZnSe in the IR, while the optical constants of the absorbing medium are representative for a metal oxide in the IR. An incident angle of 0° corresponds to normal incidence, while an angle of 90° corresponds to grazing incidence. Note that the perpendicular component, R_s , is always greater than the parallel component, R_p , except at incident angles of 0° and 90° where they are equal. By definition both R and T are unit-less fractions of the incident intensity I . When the second medium is transparent, R_p exhibits a minimum of zero at the Brewster angle. The Brewster angle is given by:

$$\tan(\theta) = n_2/n_1 \quad (9)$$

When the second medium is absorbing, R_p exhibits a positive valued minimum at the pseudo-Brewster angle. The behavior of R_p and R_s in figure 2 is representative for all cases where the refractive index of the first medium is less than that of the second medium.

This situation is known as external reflection.

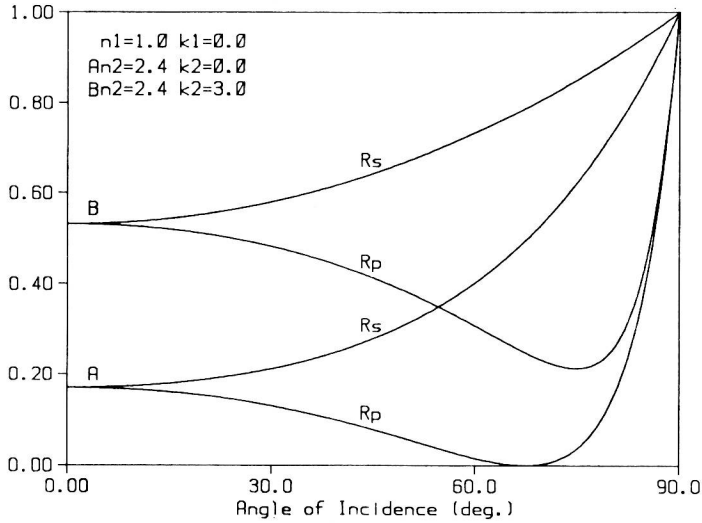


Figure 2. Reflectance as a function of incident angle for the interface between phase 1 and phase 2 where phase 1 is the incident medium. Two different interface are shown: (A) $\hat{n}_1=1.0, 0.0i$, $\hat{n}_2=2.4, 0.0i$, (B) $\hat{n}_1=1.0, 0.0i$, $\hat{n}_2=2.4, 3.0i$.

If the refractive index of the first medium is greater than the second, then total internal reflection will occur when the angle of incidence is greater than the critical angle. Below the critical angle the behavior of R_p and R_s is similar to that for external reflectance. Figure 3 shows R_p and R_s for cases where the incident medium is transparent and optically denser than the substrate medium. If the second medium is transparent, then both R_p and R_s will equal 1.0 above the critical angle, and all of the incident light is reflected. The critical angle is given by:

$$\sin(\theta_c) = n_2/n_1 \quad (10)$$

For the situation in figure 2A, R_p equals to zero at the Brewster angle (20.6°), and equals to one at the critical angle (22.0°).

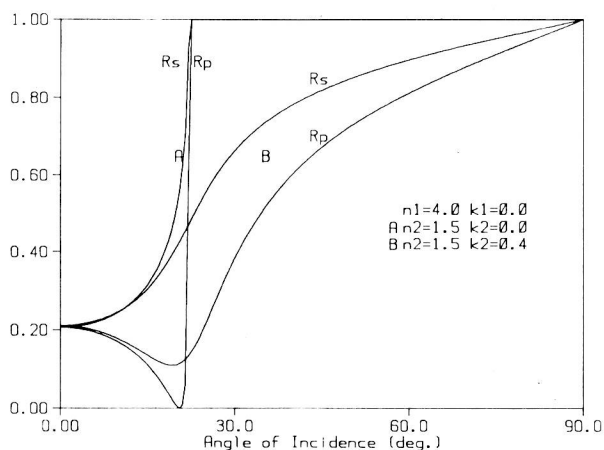


Figure 3. Internal reflectance as a function of incident angle for the interface between phase 1 and phase 2. Two different interfaces are shown: (A) $\hat{n}_1=4.0, 0.0i$, $\hat{n}_2=1.5, 0.0i$, (B) $\hat{n}_1=4.0, 0.0i$, $\hat{n}_2=1.5, 0.4i$.

If the second medium is absorbing then total internal reflection will not occur, but instead some of the incident radiation will be absorbed by the second medium. This case of attenuated total reflection is also shown in figure 3. Note, that the R_p and R_s curves have changed significantly for a relatively moderate k value of 0.4. This characteristic allows internal reflection spectroscopy to be applicable to even weak absorption bands. Typically, weak absorption bands of organic molecules in the IR will have k values in the range of 0.01-0.1, while moderate to strong bands will be in the range of 0.1-1.0. Metals are very strongly absorbing in the IR and will have k values of 10-100 across the entire mid-infrared region.

While the square of the Fresnel coefficients gives the intensity of the reflected and transmitted light at a given angle, the coefficients themselves give the amplitude and phase of the

light. The following equation relates the amplitude and phase to the reflection coefficients.

$$r_z = |r_z| \exp(i d_z) \quad (11)$$

$z = p, s$

d_z - phase change upon reflection

$|r_z|$ - amplitude of reflected light

The differential phase (Δ) and differential amplitude (ψ) for reflection are given by:

$$\begin{aligned} r_p/r_s &= |r_p|/|r_s| \exp(i(d_p - d_s)) \quad (12) \\ &= \tan(\psi) \exp(\Delta) \end{aligned}$$

$$0^\circ < \Delta < 360^\circ \quad 0^\circ < \psi < 90^\circ$$

Similar relations hold for the phase and amplitude of the transmitted light. ψ and Δ are always real and are defined on the given intervals, while r_p and r_s may be complex.

The behavior of ψ and Δ as a function of the incident angle for external reflectance is given in figure 4 where two different cases are shown. In one case both phases are transparent and Δ is 180° below the Brewster angle and 0° above it. ψ is 45° at incident angles of 0° and 90° and decreases to 0° at the Brewster angle. If the second medium is absorbing as shown in figure 4, then Δ gradually decreases from 180° at normal incidence to 0° at grazing incidence. ψ again is 45° at 0° and 90° , but does not reach 0° at the pseudo-Brewster angle.

The behavior of ψ and Δ for internal reflectance is shown in figure 5. If the first medium is more optically dense than the second, and both phases are transparent, then Δ will be 180° below the Brewster angle, 0° between the Brewster and critical angles, and will vary with incident angle above the critical angle. ψ is 45° at normal incidence and above the critical angle. ψ decreases from 45° to 0° when the incident angle changes from 0° to the Brewster angle. Between the Brewster and critical angles ψ increases rapidly from 0° to 45° . For this example the Brewster angle is 22.6° and the critical angle is 24.6° .

The phenomena of phase change for reflected or transmitted light can be used to produce elliptical or circular polarization from linear polarization. Figure 6 shows that any of these polarization states can be achieved by summing two mutually