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NOTICE

EFFECT OF CHANGES IN ABSORBER CONCENTRATION ON INFRARED REFLECTION-ABSORBANCE OF POLYMER FILMS ON METALLIC SUBSTRATES

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This paper examines the relationships between the concentration of functional groups and observable infrared reflection-absorbance (IR-RA) spectral changes and applies the findings to bisphenol-A polycarbonate (BPA-PC) on gold substrates. The paper then notes the importance of studying the mechanisms of photochemically and catalytically enhanced degradation at polymer-metal (oxide) interfaces for solar energy collection and gives the rationale for using the IR-RA technique for these studies. An apparatus is described which applies Fourier transform spectroscopy (FT-IR) for the IR-RA studies. An expression is developed showing the independence of the real and imaginary parts of the complex refractive index ($N = n - ik$) at the fundamental oscillator frequency when the frequency distribution of k can be approximated by a Lorentzian distribution. The values of k and n were determined for the polymer between 3200 and 950 cm^{-1} using an iterative calculation and experimentally determined reflectance spectra. From the optical constants determined for each functional group in BPA-PC, the sensitivity of the IR-RA measurement to changes in the functional group concentration was calculated for polymer thicknesses ranging from 10 nm to 10 μm. The optimum sensitivity is generally found at film thickness between 0.1 and 1 μm. At greater thicknesses, IR-RA spectra may be insensitive to changes in functional group concentration, and at thicknesses below 10 nm, the sensitivity is limited by instrumental signal-to-noise ratios.

An understanding of photodegradative reactions of polymers and the extent to which these reactions are influenced by a polymer/metal (oxide) interface is important for applications involving

the use of polymers to protect metallic surfaces from deterioration in outdoor service. Many such applications exist or are proposed for solar energy conversion systems [1]. For example, polymers have been used in attempts to protect reflector surfaces from exposure to sources of environmental degradation such as ultraviolet light, temperature, atmospheric gases, moisture, and abrasive particles, with the objective of maintaining the solar-weighted reflectance of the unit at a constant value. A polymer used to encapsulate a photovoltaic device may be in contact with several different surfaces including a semiconductor, grid metallization, interconnections, antireflection coating, and cover plate consisting of glass or another polymer. To protect the substrate in all cases, the bulk properties of the polymeric coating must be stable with respect to ultraviolet (UV) radiation, temperature, moisture, and atmospheric gases. However, the polymeric coating may itself contribute to an accelerated attack on the protected materials if degradative interfacial reactions change its desirable properties. Delamination at the polymer/metal interface and/or the concentration of reactive gases on the "protected surface" could be a likely result of such reactions. It is known that thermally induced oxidative degradation of certain polymers is accelerated when they are placed in contact with copper (oxide) surfaces [2,3,4]. What is not known is whether similar catalytic or synergistic effects result when the polymer is exposed to ultraviolet radiation while in contact with silver, aluminum, or other metallic (oxide) surfaces.

Realistic studies of bulk and interfacial degradation of polymers for outdoor applications must be concerned with the effects of UV radiation, temperature, temperature cycling, and atmospheric gases [5]. Experimental methods used to measure these effects should be sensitive to small chemical changes in the samples to allow examination of early degradative events and to perform the experiment in a reasonably short time. The method should permit these samples to be studied in a configuration that closely resembles their intended application. The results obtained should be reproducible and comparable to those obtained by outdoor exposure of similar samples. Finally, the analytical procedure should not itself contribute to sample deterioration and should be rapid compared to the events being observed.

Infrared reflection-absorption (IR-RA) spectroscopy was the primary technique chosen to obtain analytical information on polymer/metallic samples subjected to degradative conditions since the method is sensitive and nondestructive [6,7]. The placement of a specially designed controlled environment exposure chamber (CEEC) into a Fourier transform infrared spectrophotometer (FT-IR) makes possible the technique of IR-RA spectroscopy with control of degradative parameters in situ [8]. Thus, the equipment can collect low-noise spectra rapidly, enabling continual examination of the polymer/metal sample during exposure to several degradative parameters. The CEEC allows simultaneous control of UV exposure

4

intensity, sample temperature, and the composition of gases sur-
rounding a particular sample. Collection of IR-RA spectra takes
place with the sample in situ. The IR-RA, FT-IR method depends on
extreme sensitivity to small chemical changes in a given sample so
that the study can be brief, and so that only modestly amplified
exposures to environmental parameters are necessary to produce
detectable degradation.

The purpose of this work is to demonstrate the utility of the
method both through theoretical calculations of the relationship
between changing polymer functionality and observable IR-RA spec-
tral changes, and through presentation of experimental results
obtained using the apparatus mentioned above. The method has been
used to study several types of polymer films on various IR-reflec-
tive substrates; however, we shall use only our calculations for
films of bisphenol-A (BPA) polycarbonate on gold and aluminum
substrates to demonstrate the potential of this experimental
approach. BPA polycarbonate (BPA-PC) was chosen for initial study
since its bulk photochemistry is fairly well known [9,10], thus
permitting the validity of this in situ spectroscopic method to be
tested. Gold was chosen as a substrate on the assumption that it
is a chemically inert IR reflector, thus facilitating studies of
the bulk photochemistry of the material. Aluminum is a likely
candidate for reflector applications and is more likely than gold
to show interfacial activity with respect to the polymeric coat-
ing.

The theoretical portion of this paper provides the basis for a
definition of optimum sample thickness and polarization state of
IR radiation for the study of degradative changes in the major
functional groups of BPA-PC. Experimental results, which have
been presented elsewhere [8], demonstrate the feasibility of
collecting IR-RA spectra on a sample undergoing simultaneous
exposure to UV and a flow of gases while maintaining control of
the sample temperature. This capability represents an improvement
over previously reported methods [11] which depend upon removing
the sample from the spectrophotometer for irradiation, resulting
in loss of control over the sample temperature, environment, and
orientation. Preservation of sample orientation is particularly
important if spectroscopic accuracy is to be maintained in the
IR-RA experiment.

Theoretical Basis for the IR-RA Experiment.

Any technique having utility for the study of reaction kinet-
ics must include the capability of measuring an experimental
variable which is related to the concentration of the species of
interest as a function of time. The proportionality of IR-absor-
bance to concentration of an absorbing functionality, which is
summarized in Beer's law $A(\nu) = \varepsilon(\nu)bc$, is generally accepted.
When the measurement is performed on a sample dispersed at low

concentration in a nonabsorbing medium, interfacial reflection effects are low and a linear relationship between absorbance and species concentration is often obtained. A more complex relationship exists between IR-RA values and functional group concentration in an absorbing film on a reflective substrate. Allara et al. [12] showed that the frequencies of band maxima observed in IR-RA spectra do not necessarily correspond to the fundamental vibrational frequencies because of the influences of anomalous dispersion near the fundamental frequencies on the surface reflection measurement.

Theoretical investigations of the dependence of IR-RA intensities and frequencies on the optical constants defining the refractive index $N = n - ik$ of the materials being characterized were reported by Greenler [13,14]. A simplified ray diagram of the IR-RA experiment for a single thin film on a reflective substrate is shown in Fig. 1 [13]. Greenler [13] obtained a set of four complex equations (Fresnel equations) describing the magnetic and electric fields at each interface for a given angle of incidence, assuming parallel or perpendicular polarization. He also presented evidence for the influence of superstrate film thickness and IR incidence angle on the intensities of IR-RA spectral peaks. A similar set of Fresnel equations was utilized by Tomlin [15] for analysis of the reflectance of multilayer stacks of absorbing and/or reflective materials. We have used a computerized solution of the latter set of Fresnel equations to predict IR-RA values for radiation polarized parallel (p), perpendicular (s), or elliptical with respect to the plane of incidence.

Calculation of Reflection-Absorbance. Two different methods for calculating the reflectance-absorbance (RA) of a thin film on a reflective substrate have been reported. Greenler [13] used the relationship

$$RA = (R_o - R)/R_o , \qquad (1)$$

where R is the measured reflectance of the polymer-coated metal in air at a given frequency and R_o is the measured reflectance of the polymer-coated metal calculated with the assumption that the film is nonabsorbing ($k_2 = 0$). In practice, experimental values of R_o are obtained from the reflection spectrum of an uncoated metal sample similar to that used to produce the laminate. The form expressed in Eq. 1 then becomes analogous to a transmittance measurement. Allara et al. [12] used the form

$$RA = -\log_{10}(R/R_o) , \qquad (2)$$

which is analogous to a measured absorbance. Equation 1 is obviously the leading term of an expansion of Eq. 2.

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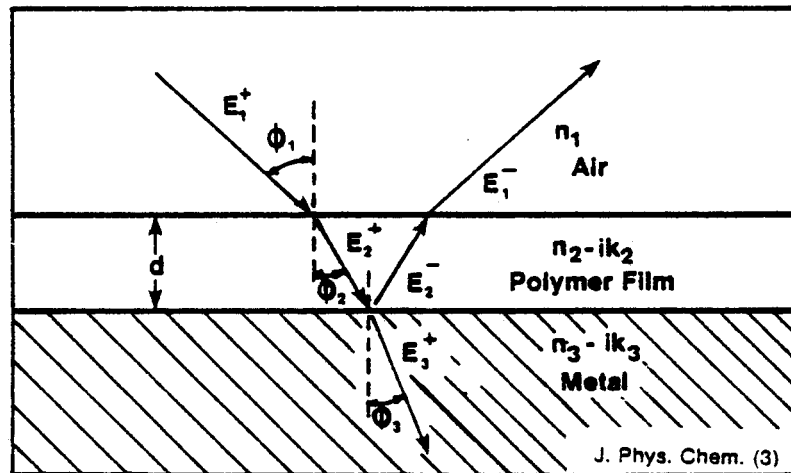
Figure 1. Ray Diagram of the IR-RA Experiment for a Polymer-Coated Metal. Adapted from work by Greenler [13]. The subscripts 1, 2 and 3 on the optical constants correspond to the electromagnetic wave in air, polymer film, and metal, respectively.

Relative Concentration of Absorbing Species. The relationship between n and k in $N = n - ik$ is of concern in RA experiments since some of the IR radiation reflected from the polymer-coated metal may have been reflected from the polymer/air interface. Thus, IR-RA measurements of relative changes in concentration (roughly proportional to changes in k) will generally be influenced by associated changes in n with a resultant loss of accuracy. However, there are exceptions to this generalization which may be elucidated by an examination of the mathematical relationship between n and k expressed in the Kramers-Kronig relations [16].

Allara et al. [12] presented a simplified version relating n and k, i.e.,

$$n(\nu_0) = n_\infty + \frac{1}{\pi} P \int_{\nu_1}^{\nu_2} \frac{k(\nu)d\nu}{(\nu - \nu_0)} \quad , \qquad (3)$$

where n_∞ represents the contribution of all other oscillators in the sample to the value of n and is usually evaluated outside the band of the oscillator under consideration defined by ν_1 and ν_2 but away from other oscillator frequencies and where P denotes the Cauchy principal value. Equation 3 is based on two assumptions: the first is that the vibrational mode having fundamental frequency ν_{max} can be modeled as an independent oscillator. The second assumption is that $\nu \gg (\nu - \nu_0)$ in the range of frequencies included in the absorption band (ν_1 to ν_2), where ν_0 is the frequency within this band at which n is evaluated. The conventions implicit in Eq. 3 are that $\nu_1 < \nu_0 < \nu_2$ and $\nu_1 < \nu_{max} < \nu_2$.

The integral in Eq. 3 may be evaluated by assuming that the k frequency spectrum within the absorption band may be approximated by a Lorentzian distribution:

$$k(\nu) = \frac{1}{\pi} \frac{\Gamma/2}{(\nu - \nu_{max})^2 + (\Gamma/2)^2} \quad , \qquad (4)$$

where Γ is the full width at half height $k(\nu_{max})/2$ of the distribution. Equation 3 can be integrated to yield Eq. 5 by using the definition of the Cauchy principal value [16] and by inserting Eq. 4 into Eq. 3, i.e.,

$$n(\nu_{max}) = n_\infty + \frac{1}{2\pi^2 A} \left[\ln \left(\frac{(\nu_2 - \nu_{max})^2}{A^2 + (\nu_2 - \nu_{max})^2} \right) \right.$$
$$\left. - \ln \left(\frac{(\nu_1 - \nu_{max})^2}{A^2 + (\nu_1 - \nu_{max})^2} \right) \right], \qquad (5)$$

where the substitutions $A = (\Gamma/2)$ and $\nu_0 = \nu_{max}$ were made prior to

the integration. It can be seen from Eq. 5 that $n(\nu_{max}) \cong n_\infty$ for $A \ll (\nu_1 - \nu_{max})^2$ and $A \ll (\nu_2 - \nu_{max})^2$. For an integration interval symmetric about ν_{max}, i.e., $(\nu_2 - \nu_{max})^2 = (\nu_1 - \nu_{max})^2$, Eq. 6 holds:

$$n(\nu_{max}) = n_\infty . \tag{6}$$

For the isolated oscillator that we are considering, the value of n is independent of the value of k at the fundamental oscillation frequency. This is shown for the idealized k - n sets plotted in Fig. 2. As the absorptivity k decreases, the values for n change everywhere except at the fundamental oscillation frequency ν_{max}. This implies that the fraction of the IR beam which is reflected from the polymer/air interface will vary as a function of changes in both k and the associated changes in n at every frequency except the fundamental oscillation frequency. The surface reflection component can make a significant contribution to the total reflected IR signal (vector E_1^- in Fig. 1), especially when unpolarized IR incident radiation is used. Therefore, since an unbiased measurement of changes in functionality concentration (changes in k) is desired, the measurement of absorbance should be performed at a frequency where n is independent of k.

The above treatment shows that for an idealized oscillator, this condition is met at the fundamental frequency, where sensitivity to changes in concentration (or k) is also highest. The fundamental frequencies may be determined experimentally either by obtaining the k spectrum using polarimetry or by obtaining the transmittance spectrum. Data resulting from application of both techniques to BPA-PC will be presented below.

Determination of Optical Constants in the IR for Bisphenol-A Polycarbonate.

The purpose of obtaining spectral data on the complex refractive index of polycarbonate polymer was to permit detailed interpretations to be made of the IR-RA spectra collected in situ on metal-backed films of this material. Several of the principal methods for obtaining the optical constants n and k of an isotropic medium have been reviewed by Humphreys-Owen [18]. All of the methods outlined are insensitive to k when k is close to zero, which is the case for frequencies between absorbance bands. For this study, a polarimetric technique (method D in Ref. 18) was chosen to obtain the optical constants of BPA-PC. To apply this method, the ratio of surface reflectances R_p/R_s at two large, but well-separated, angles of incidence (θ_i) was obtained for BPA-PC in the IR. R_p is defined as the reflectance measured for a sample using radiation polarized parallel to the incidence plane and R_s

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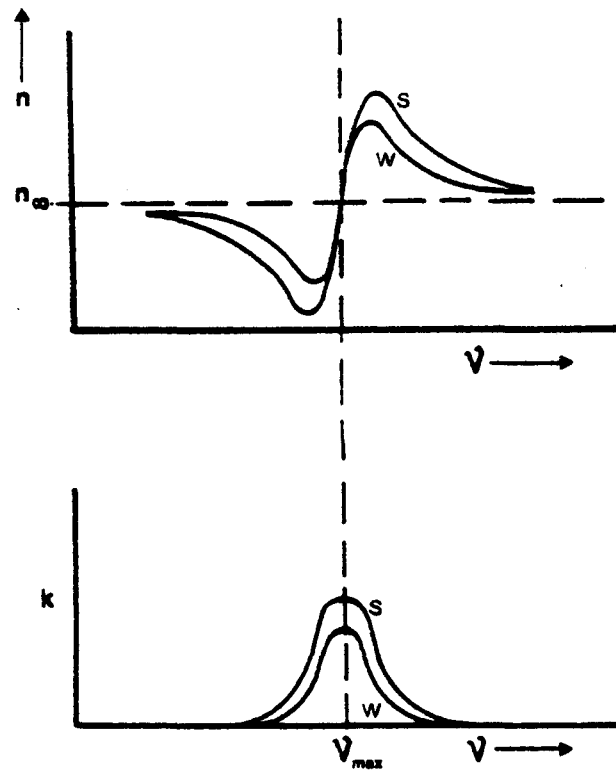
Figure 2.   Plots of n and k for Strong (s) and Weak (w) Absorption
            for Idealized Oscillators.   (Adapted from
            Nussbaum [17])

is the reflectance measured using light polarized perpendicular to this plane. Measurement of R_{θ_i}, which is the ratio of R_p/R_s, at two different values of θ ($i = 1$ or 2) yields two equations with only n and k unknown. However, the resulting two equations cannot be solved explicitly for n and k [12]. To estimate n and k, an iterative calculation is used that proceeds from trial values for n and k, values for the incidence angles used, and the corresponding measured values for the reflectance ratios, R_{θ_i}. Using the initial trial values for n and k, estimates for R_{θ_1} and R_{θ_2} are calculated at both angles of incidence, and the differences ΔR_{θ_i} between the calculated and measured values are computed. Correction factors Δn and Δk are then computed using

$$\Delta R_{\theta_i} = \left(\frac{\partial R_{\theta_i}}{\partial n}\right)_i \Delta n + \left(\frac{\partial R_{\theta_i}}{\partial k}\right)_i \Delta k \quad , \tag{7}$$

where $i = 1$ or 2. The correction factors are added to the current trial values for n and k, and the revised values become the trial values for the next iteration. Convergence is assumed to have occurred when the sum of the absolute values of Δn and Δk falls below 0.005.

According to Allara et al. [12], the ratio I/I_o of detected-to-incident radiation may be related approximately to the absorbance coefficient k by assuming that the absorption band is well isolated. Thus, the ratio becomes

$$I/I_o \cong e^{-4\pi k b \tilde{\nu}} \quad , \tag{8}$$

where b is the optical path length (cm) for absorption and $\tilde{\nu}$ is the frequency expressed in wavenumbers. This expression may be combined with the Beer-Lambert absorbance law

$$I/I_o = 10^{-\epsilon bc} \quad , \tag{9}$$

to yield an approximate relationship between k, the decidic molar absorptivity ϵ, and the molar concentration c of the absorbing species in the solid polycarbonate matrix. By combining Eqs. 8 and 9, k can be expressed as

$$k \cong \frac{2.303 \ \epsilon c}{4\pi\tilde{\nu}} \quad . \tag{10}$$

Molar absorptivities may be calculated from absorption spectra of compounds distributed uniformly at well-defined concentrations in cells of known path length, assuming that Beer's Law is obeyed.

11

Experimental Apparatus and Procedures

The major pieces of apparatus used to perform the abbreviated exposure experiment consist of an FT-IR spectrophotometer (Nicolet 7199) with a DTGS detector, a controlled environmental chamber (CEEC) with monitoring system and gas supply, and a solar simulator. The polymer-coated mirror sample is mounted inside the CEEC, which is mounted inside the sample compartment of the FT-IR. Details of the instrumentation have been presented elsewhere [8]. A schematic of the CEEC is shown in Fig. 3.

To obtain the reflectance measurements necessary to determine the optical constants of BPA-PC, a specular reflectance accessory (Harrick Scientific Co., Part No. VRA-RMA) was installed in the rear IR beam of the FT-IR. This variable-angle accessory was fitted with a kinematic mounting base and a spring-loaded sample holder to increase reproducibility of sample positioning. The latter change restricted the variability of actual incidence angle to a range of 77.5 to 60 degrees in the high-angle configuration. The incidence angles read from the angular scale on this instrument were calibrated to true values by using a laser reference beam and an aluminum mirror at the sample location. A Perkin-Elmer wire-grid polarizer consisting of gold grid elements on an AgBr substrate was used in conjunction with the specular reflectance attachment. For polymers and other substances that are partially transparent to the incident IR radiation, internal reflections may bias the measurement of surface reflectivity. To reduce this effect while maintaining planarity of the sample surface, one surface of a 3-mm thick sheet of BPA-PC was roughened using a 600-grit emery cloth. The other surface of the sheet was prepared for IR surface analysis by scrubbing with a cotton swab saturated with optical-grade ethanol. Any IR radiation that passes through such a sheet without being absorbed is scattered randomly upon striking the rear surface in addition to being displaced laterally from the optical path to the detector by ~3 mm. Thus, radiation undergoing internal reflection in the thick sheet has a very low probability of reaching the detector and interfering with the measurement of surface reflection.

A reference reflector consisting of aluminum, vacuum evaporated onto a $50 \times 25 \times 3$ mm glass optical flat, was cleaned by centrifugal rinsing with ethanol and chloroform. Single-beam IR reflection spectra of this mirror at two angles of incidence, 76.4° and 61.4° were collected and stored, each with the polarizer set at zero and 90° from the vertical, or with polarizations perpendicular (s) and parallel (p) to the incidence plane, respectively. This procedure was also used to collect the spectra for the BPA-PC sheet. To obtain good signal-to-noise ratios for the spectra collected with parallel polarization, data from 1000 scans of the interferometer were accumulated using a cooled MCT detector to yield an averaged interferogram which was then transformed into a low-noise spectrum. Spectral resolution used was 2 cm^{-1} between
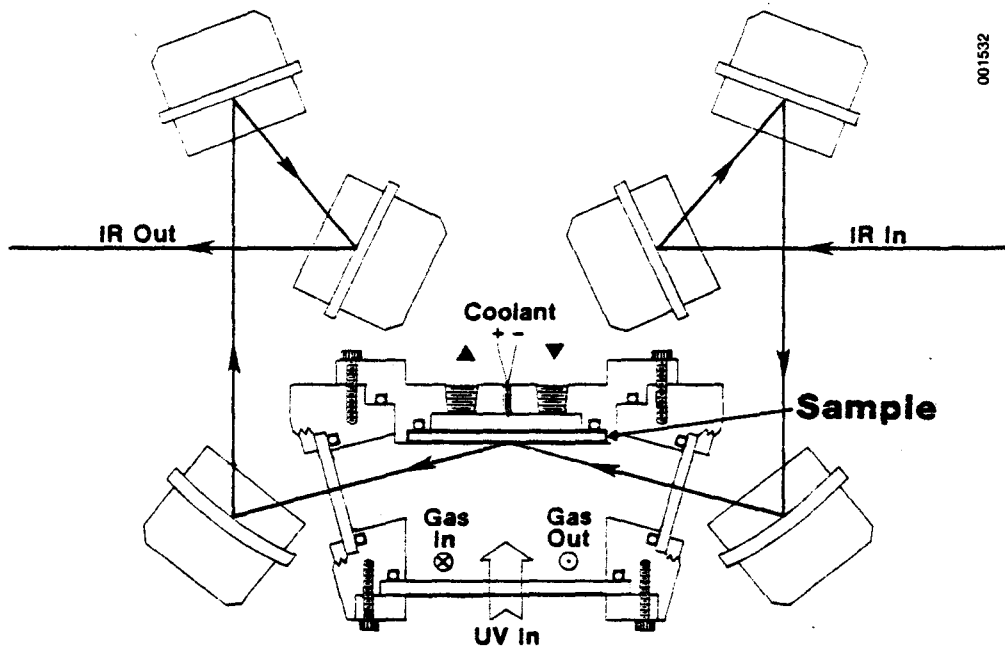
Figure 3. Controlled Environment Chamber (CEEC) Showing IR Transfer Optics

4000 and 400 cm^{-1}. The quantities R_p and R_s were determined for the two incidence angles as a function of frequency by digitally dividing each of the four reflection spectra of the polycarbonate sheet by the appropriate reflection spectrum of the aluminum reflector. The two spectral ratios R_{θ_i} (Eq. 7) were similarly generated from the four reflection spectra, and converged values for n and k were calculated.

To obtain the absorptivity coefficients of the absorbing polymer functionalities for use in predicting values of k, the IR absorption spectrum of the solid polymer was also measured. A solution of BPA-PC was prepared at a concentration of 0.105 M in reagent-grade chloroform. The absorption spectrum of this material was measured over the range 4000 - 400 cm^{-1} at 2 cm^{-1} resolution, using a cell having an effective path length of 0.0133 cm as determined by measurement of interference fringe widths. For qualitative comparison to the k spectra obtained by this method, the IR spectrum of BPA-PC was also measured using KBr discs to reduce interference fringes and solvent absorption effects. The materials were dispersed at ~5% concentration in dry KBr by solvent evaporation, subsequent grinding of the blend, and pressing into discs. Plots of the n and k spectra and the absorbance spectrum for BPA-PC are shown in Figs. 4 and 5, respectively.

Results and Discussion

In this section, the spectral optical constants measured for BPA-PC in the IR are presented first. Using these data, the relationships between IR-RA absorbance values and BPA-PC functionality concentration were determined for a range of applicable film thicknesses using an optical model of the IR-RA experiment.

Optical Constants of Bisphenol-A Polycarbonate in the Infrared.
The spectral values obtained for n and k of BPA-PC between 2000 and 950 cm^{-1} are plotted in Fig. 4. In the 3200-2800 cm^{-1} region, which encompasses the C-H stretching region of the spectrum (not shown), the expected variations in n and k were too small to be detectable above the level of random noise. A constant value of n $\approx$ 1.39 was measured within the higher wavenumber region.

From the data presented in Fig. 4, the level of random noise in the determination was estimated at ± 0.01 units for n and ± 0.05 units for k. The generally decreasing slope of the k spectrum between 2000 and 1300 cm^{-1} may result from a minor systematic error in the measurement. Such an error could be caused by increased scattering of IR radiation by the polymer sheet relative to that produced by the metallized optical flat used as a reflectance standard, or by minor misalignment of the sheet relative to the standard.

An IR absorption spectrum of the polycarbonate polymer used in these determinations is shown in Fig. 5. A comparison can be made
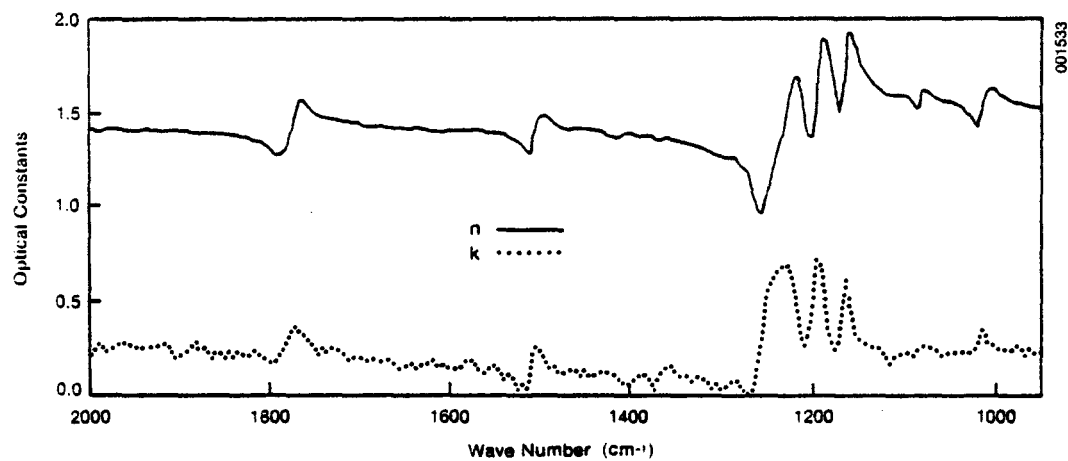
Figure 4. Real (n) and Imaginary (k) Parts of the Complex Refractive Index Calculated From Reflectance Measurements for Bisphenol-A Polycarbonate Film
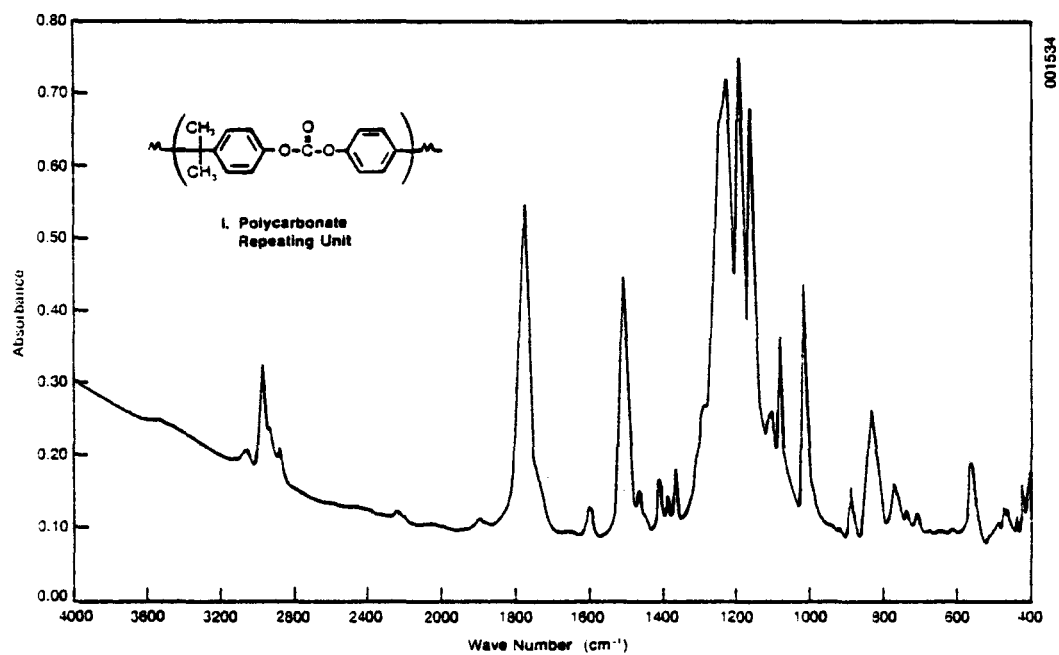
Figure 5. Absorbance Spectrum of Lexan® Polycarbonate Used for Refractive Index Determinations. The polymer was dispersed in a KBr disc at ca. 5 wt %.

between this spectrum and the k spectrum shown in Fig. 4. The major absorption bands at 1778, 1505, 1230, 1195, 1165, and 1016 cm^{-1} correspond in both shape and position, but not necessarily in relative intensities to the maxima observed in the k spectrum at 1775, 1505, 1230, 1195, 1165, and 1015 cm^{-1}, respectively. In Fig. 5, the less intense absorption bands at 2960 cm^{-1} and 1600 cm^{-1} do not have distinguishable counterparts in either the k or the n spectrum of Fig. 4, while the moderately strong absorption band at 1080 cm^{-1} has an associated variation visible in the n spectrum only. It is important to recall in this context that the intensities of the k spectral peaks are functions of frequency, as well as of absorptivity coefficient and functionality concentration, as demonstrated in the derivation of Eq. 10.

In Table 1, a comparison is made between the k values calculated using Eq. 10 and the measured maximum intensities of those peaks in the k spectrum (Fig. 4) for which structural assignments in the polycarbonate repeating unit may be made without ambiguity. The calculated k values were obtained (Eq. 10) using molar absorptivity coefficients estimated from the IR absorbance spectrum of a BPA-PC solution in chloroform. Absorptivity coefficients estimated in this manner are in good agreement with published values [19]. Similarly, the correspondence between measured and calculated k values is also fairly good. The value of k calculated using IR absorbance for the relatively weak methyl band at 2960 cm^{-1} is well below the random noise level of ±0.05 units in the k spectrum determined polarimetrically; thus, it is not

Table 1. Comparison of k Values for Various Polycarbonate Functional Groups Using Two Different Measurement Methods

Functional Group	k Spectrum Maximum (cm^{-1})	ε, Absorptivity Coefficient (ℓ mol^{-1}cm^{-1})	Bulk Concentration (M)	k (from Absorbance Measurement)	k (from Reflectance Measurements)
$-O\overset{\overset{O}{\|}}{C}$	1230	440	9.45	0.620	0.59
⬡—O	1195	360	9.45	0.521	0.59
$\overset{\overset{O}{\|}}{O}$	1775	380	4.72	0.134	0.13
—⬡—	1505	144	9.45	0.166	0.19
—CH	2960	44	9.45	0.025	--

surprising that this band is not distinguishable in the k spectrum. In utilizing Eq. 10 to predict approximate values for k, correct assignment of the absorption bands from which ϵ is calculated to the various polymer functionalities is obviously important. For example, the two absorption bands at 1230 and 1195 cm^{-1} were assigned to the two distinguishable types of C-O single bonds (inset, Fig. 5) in the polycarbonate repeating unit, on the basis that the intensities of the absorption peaks and those of the peaks in the k spectrum (corrected for frequency difference) (Figs. 4 and 5) are nearly equal. This should be the case for species having similar extinction coefficients present in equal concentrations in a polymer matrix. The intensity of the peak at 1165 cm^{-1} is significantly lower, especially in the k spectrum, and it may result from absorption by another functional group. Gupta [9] assigns this absorption to a C-C single-bond vibration.

For an independent oscillator, the validity of Eq. 6 as applied to various oscillators in the polycarbonate repeating unit may be checked with reference to the n spectrum presented in Fig. 4. Since Eq. 6 was developed with the assumption that the vibrational frequency ν_{max} was well separated from other strong absorption frequencies, an oscillator whose n spectrum conforms to Eq. 6 may be considered to be sufficiently isolated to be spectrally independent of adjacent absorbances.

In Table 2, a comparison is made between the values of n measured at ν_{max}, with values of n_{∞}^- and n_{∞}^+ estimated from measurements of n at frequencies higher and lower than ν_{max}, such that $dn/d\nu = 0$. It is apparent from an examination of Table 2 that Eq. 6 holds strictly only for the carbonyl vibration at 1775 cm^{-1} and the aromatic vibration at 1505 cm^{-1}. The $n(\nu_{max})$ value for the ester vibration at 1230 cm^{-1} also falls within a range of values defined by n_{∞}^- and n_{∞}^+; however, the width of this

Table 2. Comparison of n Values Measured
at the Fundamental Vibrational
Frequencies to Values Estimated
for n_{∞}

ν_{max}	$n(\nu_{max})$	ν_1	n_{∞}^-	ν_2	n_{∞}^+
1015	1.575	950	1.523	1055	1.558
1165	1.694	1110	1.590	1450	1.409
1195	1.652	1110	1.590	1450	1.409
1230	1.449	1110	1.590	1450	1.409
*1505	1.388	1450	1.409	1660	1.415
*1775	1.403	1650	1.415	2000	1.402

$*n(\nu_{max}) \cong n_{\infty}$

range precludes an unambiguous definition of n_∞ (Fig. 4). We infer that only the carbonyl and aromatic bands in the IR-RA spectrum are sufficiently separated from other absorption bands to enable independent concentration determinations of these polymeric functional groups to be made via RA spectroscopy. Even measurements made at these frequencies may be biased by appearance of nearby absorbances related to the buildup of reaction products during the course of irradiation.

The large variations in n observed at frequencies near the fundamental frequencies and the relationship between n and k expressed in Eq. 3, will clearly influence attempts to measure changes in concentrations of functional groups (i.e., changes in k) using the RA technique. As demonstrated in the derivation of Eq. 6, changes in k can be measured independently of the associated changes in n only at a fundamental vibrational frequency. Since the value of n changes rapidly as a function of frequency near ν_{max}, accurate determinations of ν_{max} are necessary for unbiased measurements of changes in k to be made. Since the influence of surface reflections on positions of the spectral maxima is low at normal incidence, the frequencies of the oscillators (k maxima) may be determined fairly accurately from an IR absorption spectrum of the material to be studied. The assertion of Allara et al. [12] that the positions of the IR-RA band maxima do not necessarily define the vibrational frequencies of the species of interest is reinforced by an examination of the n spectrum in Fig. 4. Therefore, integrating an absorption band to determine changes in concentration, a technique commonly used in transmission-mode experiments, may not be applicable to RA bands. Instead, useful fundamental frequencies of all species to be studied must first be determined by an appropriate transmission-mode experiment or, more accurately, by a determination of the complex refractive indices as a function of frequency. Changes in k may then be related to the changes in the absorption spectrum measured in the RA mode at these frequencies, provided that they do not overlap measurably with the vibrational frequencies of other functional groups (including those of reaction products) and that the absorbances of the materials being measured are low enough to permit good sensitivity to changes in k.

Most Useful Method for Calculating Reflection-Absorbance. IR-RA intensities calculated using both Eqs. 1 and 2 show that Eq. 2 yields good proportionality to BPA-PC functionality concentration over the widest range of polymer film thickness. Therefore, this equation was utilized in all calculations of IR-RA discussed subsequently.

Effect of p- and s-polarized Incident IR Radiation on IR-RA Intensities. The existence of an optimum polarization state for the study of thin films on reflective substrates can be demonstrated by an examination of the relative magnitudes of the IR-RA

signals predicted for p- and s-polarized IR incident radiation.
The IR incidence angle was not treated as a variable subject to
optimization; the dimensions of the spectrophotometer sample
compartment and other constraints limited the possible range of
incidence angles which could be accommodated in the CEEC. The
chosen design value of 75° was used throughout these calculations.

The optical constants for BPA-PC at the fundamental vibra-
tional frequencies were determined by application of the tech-
niques described above. Values of n_2 and k_2 measured for the
BPA-PC absorption at 1775 cm^{-1}, as well as the optical constants
for air ($n_1 = 1.0$, $k_1 = 0.0$) and for gold ($n_3 = 4.2$,
$k_3 = 27.6$ [19]), were used to predict IR-RA values at 1775 cm^{-1}
for BPA-PC films ranging in thickness from 0.01 to 10 μm on gold
substrates. Calculations were performed for both polarization
states using Eq. 2. Effects of the substrate properties on these
calculations are minor. For example, using the optical constants
of aluminum ($n_3 = 6.8$, $k_3 = 32.0$ [19]) resulted in changes of <1%
in the values obtained.

To compare the magnitudes of the reflection-absorbances
(Eq. 2) obtained using p- and s-polarization, the logarithm of
their ratio is plotted vs. film thickness in Fig. 6 This plot
affirms the conclusion made by Allara et al. [12] and
Greenler [13] that p-polarized light is at least two orders of
magnitude more sensitive than s-polarized light to absorption by
films less than 0.1 μm thick. However, it is interesting to note
that this advantage decreases rapidly for thicker films. In the
particular case illustrated in Fig. 6, s-polarized radiation would
actually yield an RA value about four times greater than would
p-polarized radiation for a 1.25 μm film. The variation in sensi-
tivity for s and p polarization and is a result of the location of
standing wave maxima and nodes in the thicker films.
Greenler [13] showed that the p-polarized electromagnetic vector
has a maximum at the film/reflector interface, while the s-
polarized vector has a node at this interface. The absorption of
s-polarized light in a 1.25 μm film probably results from inter-
actions with carbonyl groups located some distance from the
polymer/metal interface. Calculations show that p-polarized light
yields RA values (Eq. 2) that are more nearly linear with concen-
tration than does s-polarized light, probably because p-polarized
light undergoes less reflection at the polymer-air interface.

The conclusions to be drawn from these results are that, for a
75° incidence angle, p-polarized light will be more sensitive than
s-polarized light to absorbance of films less than 1 μm thick, and
p-polarized light will yield RA values more nearly linear with
respect to concentration than will s-polarized light.

**Sensitivity of the IR-RA Measurement to Changes in
Functional Group Concentration.** The experimental parameter
of polymer film thickness can be treated as a variable
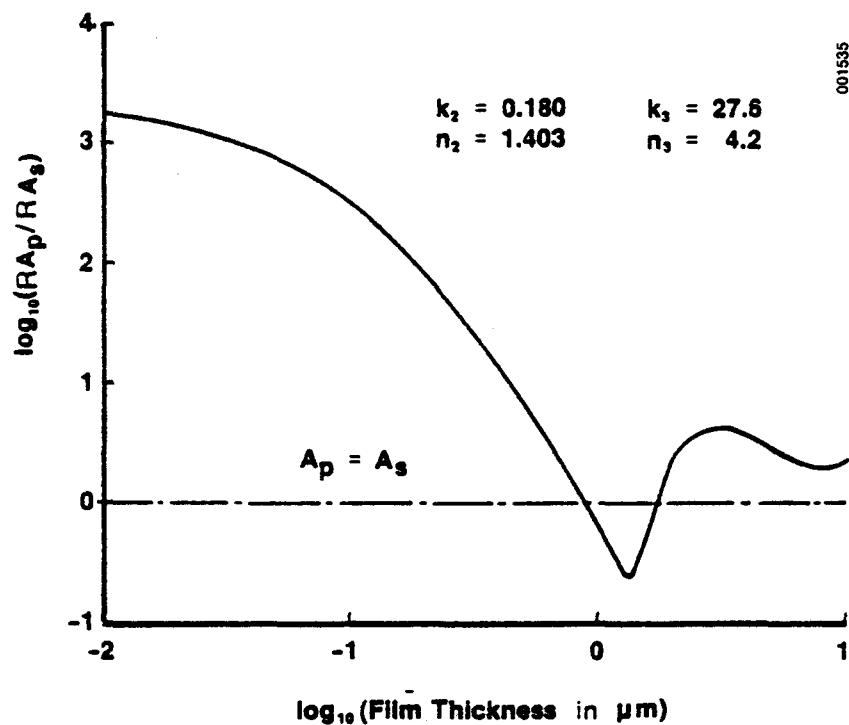subject to optimization, with the objective of obtaining a

Figure 6. Calculated Magnitudes of Relection-Absorbance Using p-Polarized Light (RA_p) Relative to That Measured Using s-Polarized Light (RA_s) for Film Thicknesses 0.01 to 10 μm. Absorbances were calculated for BPA Polycarbonate Carbonyl Absorption at 1775 cm^{-1}, assuming a gold substrate and 75° incidence Angle.

optics used in conjunction with the CEEC.

The plot for the strong carboxylic ester absorption at 1230 cm^{-1} (Fig. 8) shows an interesting variation in the relationship between absorbance and concentration for a 10-µm BPA-PC film. The measured RA values actually increase as ester concentration is decreased because nearly all of the IR signal observed for an undegraded film will be reflected from the film surface. Any light not reflected will be totally attenuated by absorption within the 10 µm film. As the value of k_2 is reduced, the predicted RA values increase because surface reflection decreases and more IR radiation is refracted into the film where it is absorbed. Only if the value of k_2 is reduced to <15% of its original value does sufficient IR radiation pass through the polymer film to permit a roughly linear relationship between RA values and ester concentration.

Calculations (not plotted) for the weak BPA-PC methyl absorption at 2960 cm^{-1} reveal that the predicted IR-RA values for a 1.0 µm film are quite linear with concentration, and deviate only moderately from linearity even for a 10.0 µm film. However, the reflection-absorbance intensity predicted for a 1.0 µm film is only 0.065 units compared to a random-noise level of ±0.0015 absorbance units for measurements made near 2960 cm^{-1}. A reduction of <9% in the methyl functionality concentration in a 1.0 µm film of BPA-PC would not be detectable (S/N > 2) using 100 scans even if p-polarized light were employed.

The sensitivity of the IR-RA technique to reductions in BPA-PC functionality concentration is summarized in Table 3. An inspection of Table 3 reveals that IR-RA measurements sensitive to the widest range of reductions in BPA-PC functional group concentrations are possible on films of about 1.0 µm in thickness. Greater linearity, with little sacrifice in sensitivity, may be obtained from measurements made at the carbonyl and ester frequencies using 0.1 µm films, but sensitivity to reductions in concentration of the methyl functional group will be reduced. Also, any technique that results in increases in signal-to-noise ratio without increasing the measurement time will extend applicability of the method to thinner films with a consequent increase in the linearity of the RA values obtained.

If estimated values of the optical constants for polymer degradation products absorbing at different frequencies than the existing polymer functionalities were available, plots for these species similar to Figs. 7 and 8 could be constructed. Such estimates could be developed from the absorbance spectra of monomeric analogs to these compounds using Eqs. 6 and 10. From these plots, the concentration changes undergone by the polymer functional groups and those of the reaction products could be estimated.

The effect of film thickness on penetration of UV radiation into the films should also be considered. If optimization of film thickness were to be based only on the predictions presented in

linear relationship between functionality concentration in the film and measured values of reflection-absorbance. Stronger IR-RA bands of optically thick films exhibit a loss of sensitivity to decreases in absorber concentration, and the weaker IR-RA bands of optically thin films exhibit an unacceptably low S/N ratio. However, an optimum film thickness may exist which will permit simultaneous study of both strongly and weakly absorbing functionalities in a given polymer.

We therefore calculated the dependence of IR-RA intensities obtained using p-polarized light at a 75° incidence angle on reductions in the initial concentration of the methyl, carbonyl, and ester functionalities at 2960, 1775, and 1230 cm^{-1} in BPA-PC films assuming thicknesses of 0.01, 0.1, 1.0, and 10.0 μm. Such reductions in functional group concentrations were modeled to be similar to those caused by degradation in actual films. The n_2 and k_2 values measured at each of the above fundamental frequencies for BPA-PC, and the above optical constants for gold and air were used to calculate the reflection-absorbance of a film having a given thickness deposited on a gold reflector. The initial value of k_2 was then reduced by successive 20% increments to correspond to degradation-related decreases in concentration of the absorbing functionality of the polymer matrix, and the RA values were calculated for the reduced k_2 values. The value of n_2 was held constant since the calculations were performed at a fundamental vibrational frequency, although, strictly speaking, Eq. 6 will be satisfied only for the well-isolated bands centered at 2960 and 1775 cm^{-1}. To facilitate display of these calculated results, the RA values predicted for a functionality at reduced concentration (i.e., reduced k_2) in a film of a given thickness were divided by the respective initial RA values. The resulting ratios are plotted as a function of the logarithm of film thickness in Figs. 7 and 8. From the plot for the moderately strong BPA-PC carbonyl absorption at 1775 cm^{-1} (Fig. 7), a radical departure from concentration linearity is observed for the RA values predicted for a 10 μm film. For such a thick film, the RA technique at 1775 cm^{-1} would be insensitive to reductions in carbonyl concentration because very little radiation will penetrate this film until its optical density has been substantially reduced (by degradation, for example). Films of 1.0 and 0.1 μm thickness are predicted to yield RA values exhibiting much better linearity with respect to carbonyl concentration. Films much thinner than 0.1 μm will yield RA values for carbonyl absorption with unacceptably low S/N ratios. Similar behavior is predicted for the BPA-PC aromatic absorption at 1505 cm^{-1}, which has a k value close to that measured for carbonyl. Noise in this spectral region, which is about ± 0.001 absorbance unit for the 100 scans employed for signal averaging, could be reduced by collecting more scans, but time resolution in these studies of reacting systems would be sacrificed. Noise could be reduced more effectively by utilizing a cooled detector or by improving the throughput of the IR transfer
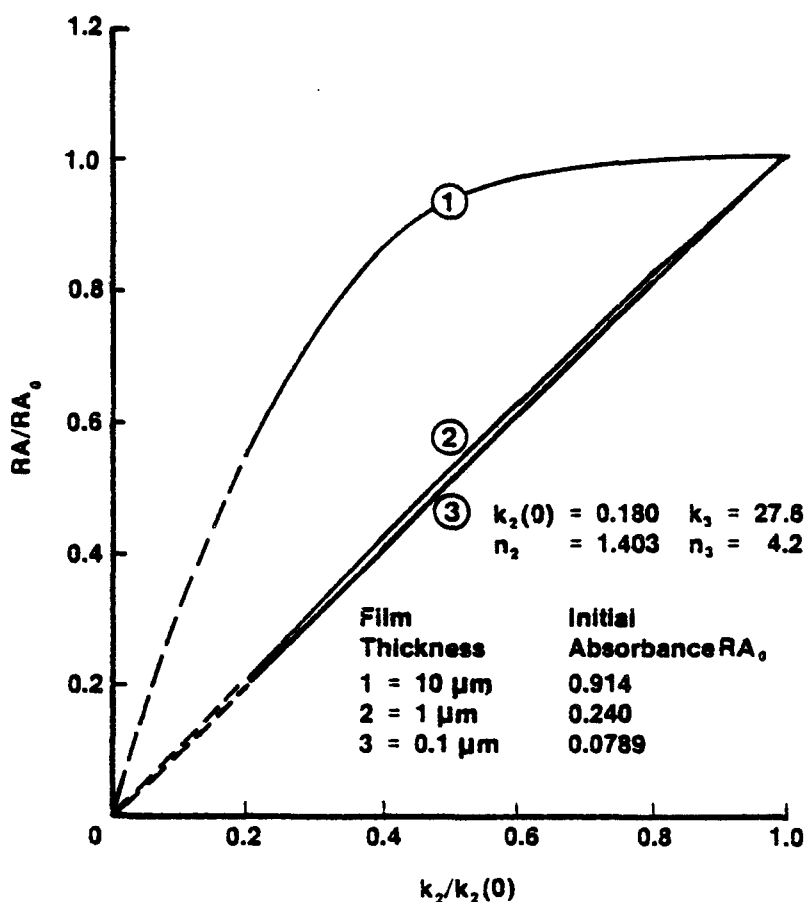
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Figure 7. Sensitivity of Reflection-Absorbance (RA) to Decreases
in k at 1775 cm^{-1} of BPA polycarbonate. The
absorbances were calculated for various thicknesses of
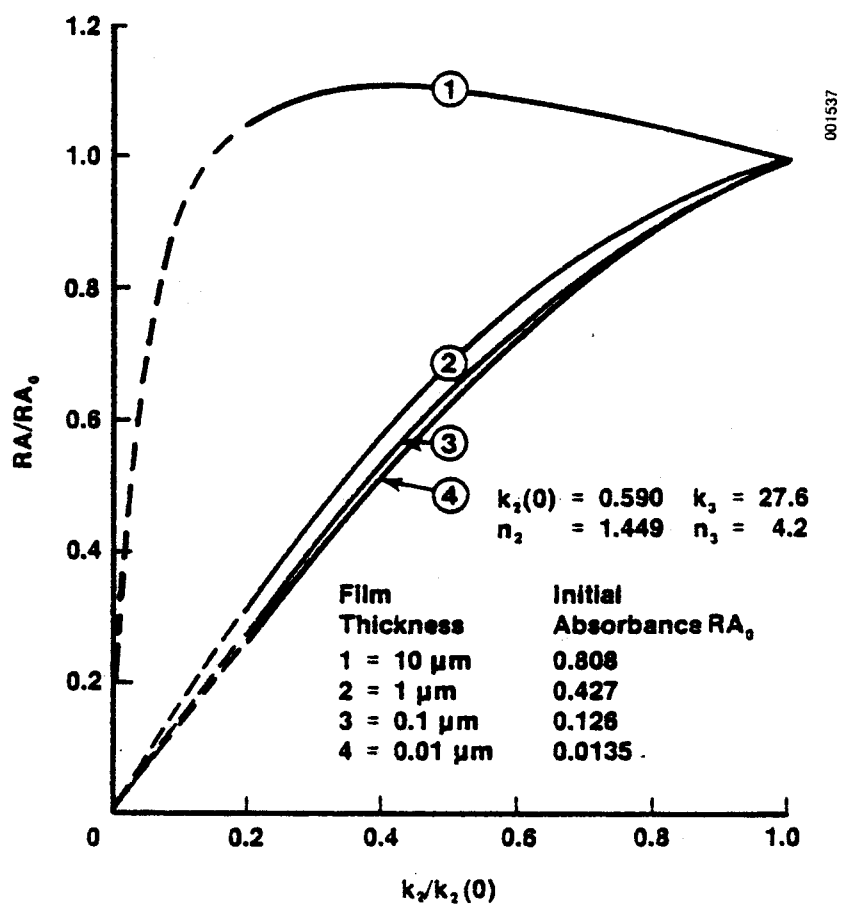PC films on gold substrates, assuming p-polarized light
at a 75° incidence angle.

001537

Figure 8. **Sensitivity of Reflection–Absorbance (RA) to Decreases in k (at 1230 cm^{-1}) of BPA Polycarbonate.** The absorbances were calculated for various thicknesses of PC films on gold substrates, assuming p-polarized light at $75°$ incidence angle.

Table 3, preferential use of 10-μm films to study changes in methyl group concentration might be recommended. However, the optical model presented here assumes that the concentrations of the IR-absorbing species are uniform throughout the film. Therefore, if the bulk concentrations predicted by the optical model are to be valid throughout the film, degradative reactions should occur uniformly throughout the film. For reactions influenced by the metallic substrate, this requirement will obviously be met better by thinner films. Also, for photochemical reactions to yield degradation products that are distributed uniformly throughout the film, the intensity of UV radiation throughout the film must also be uniform. This condition likewise will be most nearly approximated in thin films.

Table 3. Sensitivity of the IR-RA Measurement
to Reduction in Initial Concentration
of Several Functional Groups in
Bisphenol-A Polycarbonate Films of
Various Thicknesses*

Functional Group	Film Thickness, μm			
	0.01	0.1	1.0	10.0
Methyl	Poor	20%	9%	3%
Carbonyl, Aromatic	Poor	3%	1%	Poor
Ester	Poor	6%	3%	Poor

*Percentages represent minimum concentration changes detectable by an IR-RA signal change having S/N = 2 using 100 Scans by the DTGS Detector

In the case of BPA-PC, some of the reaction products have much higher absorption cross-sections than the undegraded polymer at the UV wavelengths responsible for photodegradation. Gupta et al. [9] reported a value of 7300 ℓ mol^{-}cm^{-1} for the absorption coefficient of phenyl salicylate at 322 nm. The implication is that, as photodegradation produces UV-absorbing groups on the polymer chain, buildup of degradation products will eventually be restricted to the surface of the polymer film, and UV photon flux at the polymer/metal interface will be limited. The present model may be extended to account for these effects, but the most straightforward procedure is to use thin films in these studies.

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