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Monitoring Degree of Cure and Coating Thickness of Photocurable Resins
Using Fluorescence Probe Techniques

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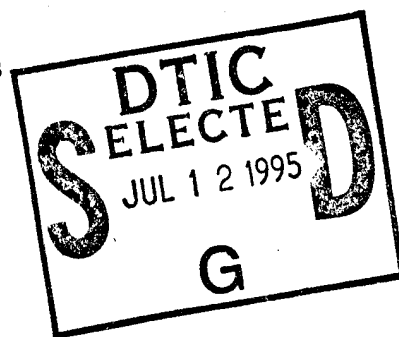
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13. ABSTRACT (Maximum 200 words)

In this paper, we report recent progress in developing fluorescence probe technology for photocurable coatings. Intramolecular charge transfer (ICT) fluorescence probes based on derivatives of dansyl amide were found to be useful for monitoring cure of various photocurable resins the polymerization of which was initiated with UV or visible initiators. Fluorescence emission spectra of chosen ICT probes exhibited spectral blue shifts due to the increases in microviscosity surrounding the probe molecules as the photocuring process proceeded. A fluorescence intensity ratio method was used to follow the probe spectral changes as a function of the degree of polymerization. Linear correlation plots between the intensity ratios as measured from the probe fluorescences and the degree of cure were obtained for varieties of photocurable resins with UV or visible initiators. In addition, a fluorescence probe technique for measuring coating thickness based on the nascent fluorescence from coating substrate is also described.

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Monitoring Degree of Cure and Coating Thickness of Photocurable Resins Using Fluorescence Probe Techniques

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Abstract

In this paper, we report recent progress in developing fluorescence probe technology for photocurable coatings. Intramolecular charge transfer (ICT) fluorescence probes based on derivatives of dansyl amide were found to be useful for monitoring cure of various photocurable resins the polymerization of which was initiated with UV or visible initiators. Fluorescence emission spectra of chosen ICT probes exhibited spectral blue shifts due to the increases in microviscosity surrounding the probe molecules as the photocuring process proceeded. A fluorescence intensity ratio method was used to follow the probe spectral changes as a function of the degree of polymerization. Linear correlation plots between the intensity ratios as measured from the probe fluorescences and the degree of cure were obtained for varieties of photocurable resins with UV or visible initiators. In addition, a fluorescence probe technique for measuring coating thickness based on the nascent fluorescence from coating substrate is also described.

Introduction

Photopolymerization, a process of converting liquid monomers or oligomers into solid polymers using UV or Visible light, has found increasing applications especially in the coating industries because of its speed, efficiency and solvent-free nature. The ultimate chemical and physical properties of the photopolymer coatings formed by photopolymerization processes depend on various factors, such as monomer structure, forms of initiation, reaction conditions and the rate and degree of polymerization. However, the industrial processing cycles of these coating resins have generally been developed empirically, by "trial and error", because of the lack of proper techniques to monitor the changes in chemical and physical properties as they occur during the processing. Resins with significant "batch to batch" variations in composition are processed using the same general curing cycle, resulting in products with significantly differing properties. Thus off-line as well as on-line cure monitoring techniques are essential for property control and processing optimization of the final products produced by photopolymerization. Several methods have been previously developed to study the kinetics of photopolymerization. Among these are differential scanning calorimetry (DSC) and photo-differential scanning calorimetry (PDSC)[3,4,5,6], laser interferometry,[7] photoacoustic spectroscopy,[8] and UV and FTIR spectroscopy.[9,10,11] DSC and PDSC are useful for studies of the kinetics of photopolymerization. The degree of cure of the resin systems can be determined from the residual heat of reaction of the unreacted functionalities. However, both DSC and PDSC are destructive techniques and therefore are not suitable for on-line cure monitoring applications. FTIR is the most utilized spectroscopic method for degree of cure measurement by monitoring changes of the characteristic monomer or polymer absorption bands. Recently, a real time

infra-red (RTIR) technique was developed to monitor the polymerization process continuously and rapidly in real time.[9,10,12] Both the rate and degree of polymerization can be measured. However, IR techniques can only be used to analyze thin films (less than 20 μm thick). They are not useful for monitoring polymerization of coatings on opaque substrates.

Fluorescence spectroscopy has been recognized as a powerful analytical technique for polymer analysis because of its sensitivity, selectivity and non-destructive characteristics. Remote and on-line sensing can be readily achieved via a fiber-optic fluorimeter with today's fiber optic technology. The performance of a fluorescence technique depends to a large extent on the properties of the fluorescence probes employed. Generally, there are two types of fluorescence probes according to their reactivities: reactive probes and non-reactive probes. Reactive fluorescence probes can be aromatic monomers or curing agents that can take part in a polymerization process. The fluorescence characteristics of a reactive fluorescence probe changes as it reacts with other components in the polymerizing system. For instance, the fluorescent excitation spectra of aromatic diamine curing agents such as 4,4'-diaiminodiphenyl sulfone (DDS) and 4,4'-diaminodiphenylmethane (DDM) were found to exhibit significant spectral red shifts during their curing reactions with epoxides, as a consequence of the conversion of the primary amines to the secondary and tertiary amines.[13] The fluorescence excitation spectral peak positions of these aromatic diamine curing agents were found to correlate well with the degree of cure. Reactive probes can also be extrinsic probes added to the polymerization systems.[14] Non-reactive fluorescence probes are useful for polymer cure characterization because of their viscosity-dependent characteristics which arises from the dependence of the internal rotations of the probe molecules to the local viscosity or microviscosity.[15] The photophysical properties of the probes can be

correlated to the degree of polymerization which affects the microviscosity surrounding the probe molecules. Several cure monitoring methods have been developed including excimer fluorescence,[16] fluorescence polarization,[16,17] fluorescence quenching,[18] time-resolved fluorescence[19] and fluorescence recovery after photobleaching.[20]

Fluorescence Probes for Photopolymerization Studies

During the last few years, our laboratories has devoted considerable efforts to develop fluorescence probe techniques for monitoring photoinitiated polymerization. Our approach has been to use viscosity-sensitive probes such as excimer forming molecules and intramolecular charge transfer complexes in which the fluorescence quantum yield and/or the fluorescence emission peak maximum are related to an intramolecular rotation-dependent relaxation process.

Excimer forming molecules such as pyrene and its derivatives exhibit dual fluorescence emissions in which the shorter wavelength band corresponds to the monomeric emission and the longer wavelength band to that of the excimer. The fluorescence intensity ratio (I_m/I_e) of the monomer emission and the excimer emission is sensitive to the changes in the microviscosity surrounding the probe and thus can be correlated with the degree of polymerization. However, a major disadvantage in using excimer probes is that large concentrations of the probes are required to form excimers, and this can limit the possible depth of observation and interfere with the photoinitiating process.[21]

Certain aromatic compounds with donor-acceptor structures such as 4-(N,N-dimethylamino)benzonitrile (DMABN) and 4-(N,N-dimethylamino) benzoate exhibit dual fluorescence emission bands corresponding to two different excited state conformations due to internal twisting.[22] The short

wavelength band is due to a coplanar (parallel) excited state conformation and the long wavelength band originates from a perpendicular conformation which is the so-called twisted intramolecular charge transfer (TICT) state. The perpendicular conformation usually exhibits an energy minimum at the excited singlet state due to a larger degree of charge separation. In contrast, the ground state exhibits an energy maximum at the perpendicular conformation. Thus, upon excitation, a molecule with a coplanar ground-state conformation will spontaneously twist toward the more stable perpendicular excited-state conformation.[23] The rate of twisting and the population of the TICT state is expected to be strongly dependent on the microenvironment of the probe molecule. Our interests were in using TICT molecules as fluorescence probes for photopolymerization studies. A number of intramolecular charge transfer probes have been evaluated for probing the degree of polymerization of polyolacrylates photopolymerized using visible initiators.[24,25,26,27] Among them are 5-dimethylamino-1-naphthalene sulfonamide (dansylamide, DA), 2-dimethylamino-5-naphthalene-n-butyl-sulfonamide (2,5-DASB), N-(4'-cyanophenyl)-carbazole (CBC), N-(4'-butyl benzoate)-carbozole (BBC), N-(1'-naphthyl)-carbazole (NNC) and 9,9'-dianthryl (see Chart 1). Dansyl amide and 2,5-DASB were successfully employed as fluorescence probes for visible light initiated polymerization. Among other probes, N-(1'-naphthyl)-carbazole was found to be the most sensitive while 9,9'-dianthryl was the least sensitive probe.[27]

To search for intramolecular charge transfer probes with large Stokes shifts and high fluorescence quantum yields, we investigated several probe compounds which were 1,5-derivatives of dansyl amide. The 1,5-isomers of dansyl amide were found to exhibit larger Stokes shift than the 2,5-isomers. For example, the Stokes shift value of 5-dimethylaminonaphthalene-1-sulphonyl-n-

butylamide (152 nm) is twice of that of 5-dimethylaminonaphthalene-2-sulphonyl-n-butylamide (76 nm) when measured in THF at room temperature.[28] Thus we focused on the 1,5-isomers of dansyl amide derivatives. Among them are 5-dimethylaminonaphthalene-1-sulphonyl-n-butylamide (DASB), 5-dimethylaminonaphthalene-1-sulphonyl-di-n-butylamide (DASD), 5-dimethylaminonaphthalene-1-sulphonyl-aziridine (DASA) and 5-dimethylaminonaphthalene-1-sulphonyl-pyrolidone (DASP) (see Chart 2). All four of the probes exhibited large values of Stokes shift of about 150-160 nm (in THF solution), as shown in Figure 1. Intramolecular charge transfer fluorescence probes with large Stokes shift values are advantageous to use for cure monitoring applications since they can provide wider spectrum windows in which to operate as well as higher sensitivities. DASB and DASD were found to be more fluorescent that DASA and DASP.[29] In this paper, we will focus on studies of the applicability of DASB probe for cure monitoring applications. Evaluation of other probes is now in progress and will reported soon.

Cure Monitoring Device

Since it usually takes time to acquire a fluorescence spectrum using a scanning emission monochromator and PMT detecting system, a conventional fluorimeter is not suitable for monitoring spectral changes of ICT fluorescence probes during a rapid photopolymerization process. Conventional fluorimeters are comprised of, mainly, a light source, an excitation monochromator, an emission monochromator, a photomultiplier tube (PMT), a data station and a recorder. Remote sensing can be achieved by using a bifurcated fiber-optic cable.

One way to shorten the spectral acquisition time is to use multiple detection heads at various emission wavelengths. For example, by using a pair of photomultiplier tubes with narrow-band interference filters and trifurcated

fiber optic bundles, Neckers et al. developed a real time cure monitoring device for laser-induced photopolymerization.[24] The fluorescence intensity ratio of two selected emission wavelengths can be monitored continuously, in real time, as the polymerization occurs. However, this system is not capable of recording a full spectrum rapidly. To overcome this difficulty, a fast detection system featuring a multichannel analyzer and a CCD detector was developed by SGL/Oriel Instruments for radiation cure monitoring applications. With this system, the spectral acquisition time can be as short as 25 ms, so a full emission spectrum can be obtained instantaneously. Using a bifurcated optic-fiber sampling technique, this device can be readily used for both on-line and off-line cure monitoring needs.

Fluorescence Intensity Ratio Method for Photopolymerization Studies

When using intramolecular charge transfer fluorescence probes to monitor photopolymerization, the probe molecules are doped into the uncured resin systems at small concentrations (0.01-0.02 wt%). As the curing reaction proceeds, the probe fluorescence emission spectral peak position generally exhibits spectral blue shifts due to the increasing microviscosity surrounding the probe. For example, a total spectral shift of about 26 nm was observed from 5-dimethylamino-1-naphthalene-sulphonyl-n-butylamide (DASB) in a acrylic coating formulation when the degree of cure increases from 0% to 87%. (Figure 2). To quantitatively monitor the spectral changes as a function of the degree of cure, we used a fluorescence intensity ratio method in which fluorescence intensities at two different emission wavelengths were ratioed. Thus, any variations in probe concentration, sample thickness and lamp intensity are internally calibrated. We found that the intensity ratio method was more

sensitive and accurate than monitoring the emission peak position since fluorescence emission spectra are generally broad and structureless.

To utilize the fluorescence probe information acquired, one needs to establish a correlation between the fluorescence response and polymer properties. One example, the measure of the degree of cure which has been determined independently using FTIR or DSC, has been particularly investigated.[30] For acrylic resins, we used FTIR to monitor the rate of disappearance of the acrylic C=C functionality. The degree of cure (α) was calculated using the following equation.

$$\alpha = 1 - \frac{A_{acry}(t) * A_{ref}(0)}{A_{acry}(0) * A_{ref}(t)} \tag{1}$$

where $A_{acry}(t)$ and $A_{acry}(0)$ are the absorbances at 810 cm^{-1} due to the acrylate double bond, after curing times t and zero, respectively. $A_{ref}(t)$ and $A_{ref}(0)$ are the reference peak absorbances at 2945 cm^{-1} due to the CH groups, after curing times t and zero, respectively. This reference peak was used as an internal standard to calibrate any thickness fluctuation during the curing process.

For unsaturated polyester resins, we found it was difficult to use FTIR to monitor the curing processes due to peak overlapping in the infrared. Thus we used differential scanning calorimetry (DSC) instead. The degree of cure (α) was calculated using the following equation.

$$\alpha = 1 - \Delta H_{residue} / \Delta H_{total} \tag{2}$$

where $\Delta H_{residue}$ is the residual heat of reaction measured for the sample after curing for a period of time. ΔH_{total} is the total heat of reaction obtained when benzoyl peroxide (1.0 wt%) was used as the thermal initiator.

Figure 3 compares the fluorescence and FTIR cure monitoring profiles of an acrylic coating formulation (Durethane low gloss coating from the PPG Industries) as a function of irradiation time using a medium pressure mercury lamp. It can be seen, the two cure profiles are about the same and a linear correlation curve between the fluorescence intensity ratios and the degree of cure was obtained as shown in Figure 4.

We have examined the applicability of DASB probe to a number of commercial UV coating formulations including urethane acrylates, epoxy acrylates, silicone acrylates and polyester acrylates.[28,29,30] In all cases, linear correlation curves between the fluorescence intensity ratios and the degree of cure were obtained. The slopes of the correlation curves were found to vary from 2.3 to 4.8, while the intercepts ranged from 1.2 to 1.6 (see Table 1). These differences probably reflected the differences in network structures of these resins.

DASB has also been successfully used to monitor photopolymerization processes initialized by visible initiators such as fluorone dye/amine or fluorone dye/onium salt/amine systems developed in our laboratories.[31] A photocurable multifunctional acrylate resin system made of trimethylopropane triacrylate (40 wt%), dipentaerythrytol monohydroxyl pentaacrylate (40 wt%) and polyethylene glycol diacrylate (20 wt%) was employed as the standard resin. The visible photoinitiator was 5,7-diiodo-3-butoxy-6-fluorone (5×10^{-4} M) with N-phenyl glycine (5×10^{-2} M) as the coinitiator. The photoinitiating mechanism (Scheme 1) is believed to be involving an electron transfer process in which the amine coinitiator donates an electron to the triplet excited state of the dye molecule. A subsequent proton transfer process will then generate an amine radical which initializes radical polymerization and a dye radical which is further reduced by hydrogen abstraction or termination.[32] So the dye is bleached to leuco form.

Before the bleaching process was completed, the fluorone dye, DIBF, was found to exhibit weak fluorescence emissions which could interfere with the measurement of the probe fluorescence signals. However, because of the probe's high fluorescence quantum yield, no significant interference was noticed. In fact, the cure profiles observed by fluorescence probe and FTIR techniques were very similar as shown in Figure 5. The probe fluorescence intensity ratio (I_{470}/I_{560}) of DASB was correlated linearly with the extent of C=C conversion determined by FTIR as shown in Figure 6.

DASB was also used to monitor visible light curing of commercial resins such as polyester acrylate and unsaturated polyesters. For photoinitiation, a "hybrid" three-component initiating system consisting of a fluorone dye initiator, 5,7-diiodo-3-butoxy-6-fluorone (DIBF), an onium salt, 4-octyloxyphenyliodonium hexafluoro antimonate (OPPI) and N,N'-dimethylamino-2,6-diisopropylaniline (DIDMA) was used with a molar ratio of 1/2/3. Even though the presence of onium salt was found to have some quenching effect on the fluorescence emission intensity of the DASB probe, linear correlation between the fluorescence intensity ratio and the degree of cure was obtained.[30] This showed one of the advantages of using the fluorescence intensity ratio method which is independence of the probe concentration.

Figure 7 shows an example of linear correlation curve for one of the unsaturated polyester resins (from Owens-Corning Fiberglass) cured with the three-component "hybrid" visible initiator (DIBF/OPPI/DIDMA). The degree of cure in this case was obtained using DSC. Therefore, the fluorescence probe technique correlated well with both FTIR and DSC techniques.

Fluorescence Method for Measuring Coating Thickness

In addition to measuring the degree of cure of a photocurable coating, we have also developed a fluorescence probe technique to determine the thickness of a coating based on nascent fluorescence from its coating substrate. Because of its high sensitivity, we expected that fluorescence probe technique could be useful for coating thickness measurement by taking advantage of the nascent fluorescence emission from the substrate through an emission (from the substrate)-absorption (by the coating layer) mechanism. By doping a fluorescence probe that can absorb the nascent fluorescence emission from the substrate, the intensity of the nascent fluorescent emission signal observed from the substrate is expected to be inversely proportional to the coating thickness. Most coating substrates such as plastics, wood, paper and glass exhibit fluorescence emission when irradiated with a UV light source, thus enabling the measurement of the coating thickness. For example, we found that nascent fluorescence emission from polyethylene teraphthalate (PET) could be used to determine the coating thickness of a silicone acrylate coating doped with a small amount of DASB probe (C=0.0005 M). When exciting at 302 nm, the nascent fluorescence emission intensity at 380 nm was found to decrease linearly as the coating thickness increased. Figure 8 shows correlation curves between the fluorescence ratio ($I_{coated}/I_{uncoated}$) and the coating thickness for PET bottles coated with a silicone acrylate doped with DASB probe. Two sections of the bottle were examined. It is understandable that the coatings on the shoulder section are generally thicker than the side section.

Summary

A fluorescence probe technique for cure monitoring of photocurable coatings was developed based on intramolecular charge transfer fluorescence

probes such as 5-dimethylaminonaphthalene-1-sulphonyl-n-butylamide (DASB) and other dansyl amide derivatives. Fluorescence emission intensity ratio of DASB probe at two different emission wavelengths were found to be correlated linearly with the degree of cure for varieties of photocurable resins with UV or visible initiators. The thickness of a polymeric coating can also be measured by taking advantages of nascent fluorescence emissions from coating substrates such as plastics, paper, wood or glass. Therefore, both the degree of cure and coating thickness of a polymeric coating can be determined using fluorescence probe techniques. Both on-line and off-line analysis can be achieved using commercial available fiber-optic fluorescence cure monitoring devices.

Table 1. Slopes and intercepts of the correlation curves between the probe fluorescence intensity ratio and the degree of cure for different UV coatings using DASB as the fluorescence probe

Resin System	Intercept	Slope
Acrylic Coating for Fibers (Primary)[a]	1.380	2.631
Acrylic Coating for Fibers (Secondary)[b]	1.628	2.320
Acrylic Coating for Vinyls (Alpha Gloss)[c]	1.447	2.654
Acrylic Coating for Vinyls (Low Gloss)[d]	1.241	2.714
Silicone Acrylate[e]	1.338	4.817

Notes: (a). An UV curable acrylic formulation (Desotech 950-076) from DSM Desotech Inc., Elgin, Illinois.

(b). An UV curable acrylic formulation (Desolite 950-044) from DSM Desotech Inc., Elgin, Illinois.

(c). An UV curable acrylic formulation (Durethane 602Z70) from PPG Industries, Inc., Allison Park, PA.

(d). An UV curable acrylic formulation (Durethane 509Z70) from PPG Industries, Inc., Allison Park, PA.

(e). An UV curable silicone acrylic formulation (Trade Code: UV 8550-D1) from GE Silicones, Waterford, NY.

Chart 1. Fluorescence Probes Used Previously For Photopolymerization
Studies
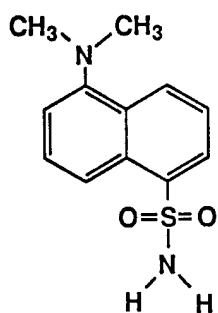
(Dansyl amide)
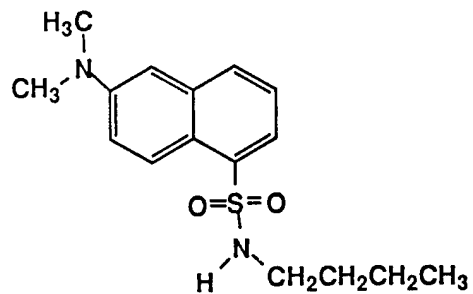
(2,5-DASB)
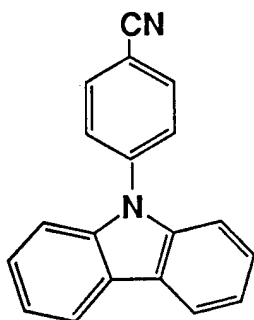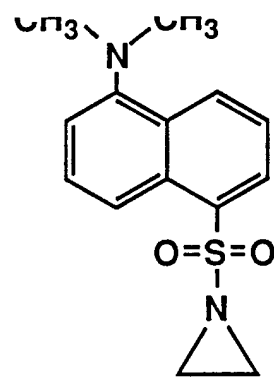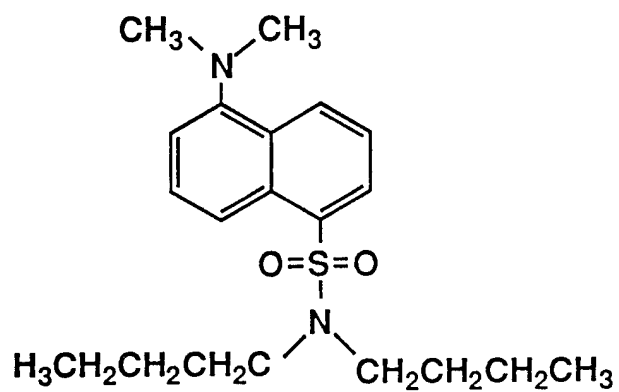

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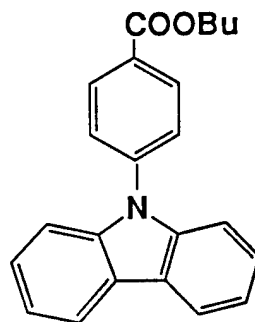
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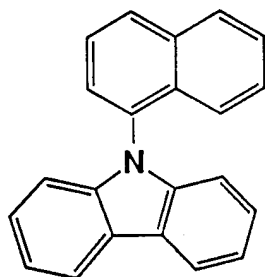
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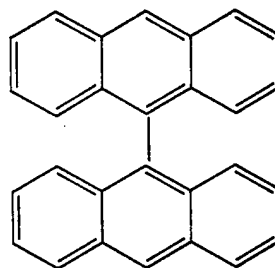
(DAN)

Chart 2. Fluorescence Probes Based on Dansyl Amide Derivatives with
Large Values of Stokes Shifts
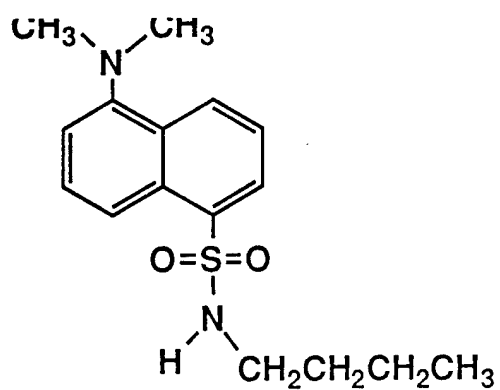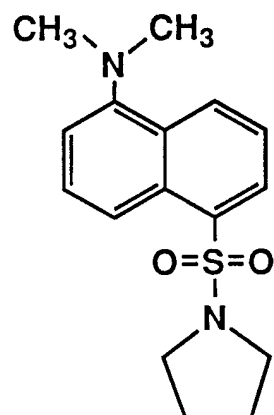

(DASB)

(DASA)

(DASD)

(DASP)

Scheme 1. Initiating Mechanism of a Fluorone Dye (DIBF)/Amine
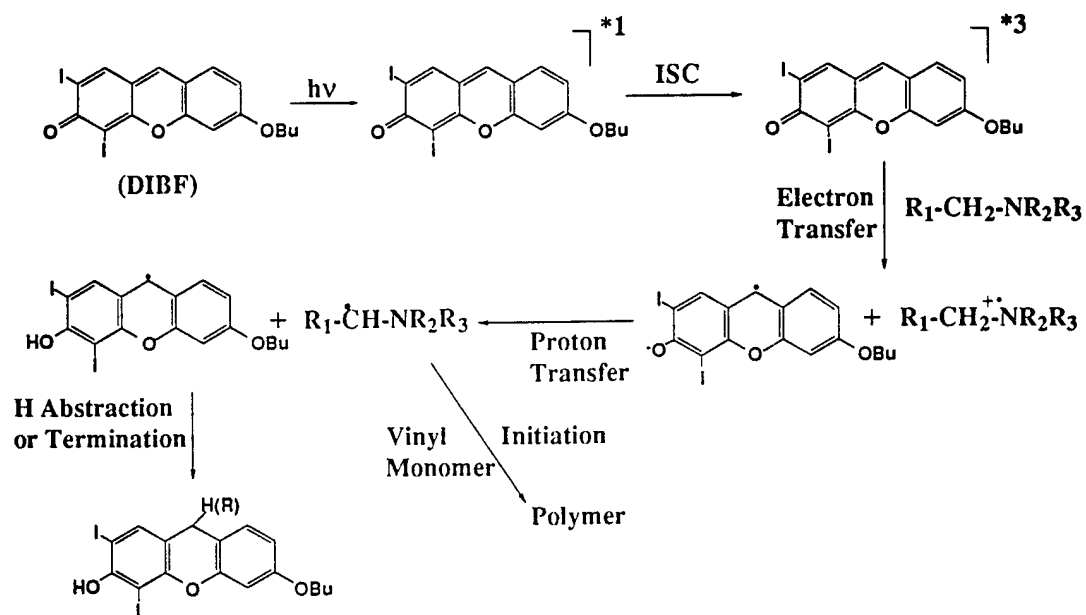Radical Initiating System (from Ref. 32)

(DIBF)

Electron Transfer | $R_1\text{-}CH_2\text{-}NR_2R_3$

H Abstraction
or Termination

Proton Transfer

$+ \; R_1\text{-}\overset{\bullet}{C}H\text{-}NR_2R_3$

$+ \; R_1\text{-}CH_2^{+\bullet}\text{-}NR_2R_3$

Vinyl Monomer

Initiation

Polymer

Figure Captions:

Fig. 1. Fluorescence excitation and emission spectra of several dansyl amide
derivatives, 5-dimethylaminonaphthalene-1-sulphonyl-n-butylamide
(DASB), 5-dimethylaminonaphthalene-1-sulphonyl-di-n-butylamide
(DASD), 5-dimethylaminonaphthalene-1-sulphonyl-aziridine (DASA) and
5-dimethylaminonaphthalene-1-sulphonyl-pyrolidone (DASP). (Solvent:
THF).

Fig. 2. Comparison of the fluorescence emission spectra of the DASB probe in an
UV curable acrylic coating formulation (Durethane low gloss coating,
from the PPG Industries) as a function of the degree of cure. (Excitation at
380 nm).

Fig. 3. Comparisons of fluorescence (a) and FTIR (b) cure monitoring profiles as a
function of irradiation time using a medium pressure mercury lamp for an
UV curable acrylic coating formulation (Durethane low gloss coating,
from the PPG Industries).

Fig. 4. Linear correlation curve between the fluorescence intensity ratio
(I_{470}/I_{560}) of the DASB probe and the extent of C=C conversion for an
UV curable acrylic coating formulation (Durethane low gloss coating,
from the PPG Industries).

Fig. 5. Comparisons of fluorescence (a) and FTIR (b) cure monitoring profiles as a
function of irradiation time for a multifunctional acrylate formulation

containing TMPTA (40 wt%), DPHPA (40 wt%) and PEGA (20 wt %) with a visible initiating system. ([DIBF] = 5×10^{-4} M; [NPG]= 5×10^{-2} M; [DASB] = 0.015 wt %; Excitation at 380 nm).

Fig. 6. Linear correlation plot between the fluorescence intensity ratio (I_{470}/I_{560}) of the DASB probe and the extent of C=C conversion for a multifunctional acrylate formulation containing TMPTA (40 wt%), DPHPA (40 wt%) and PEGA (20 wt %) with a visible initiating system. ([DIBF] = 5×10^{-4} M; [NPG]= 5×10^{-2} M; [DASB] = 0.015 wt %; Excitation at 380 nm).

Fig. 7. Linear correlation plot between the fluorescence intensity ratio (I_{510}/I_{600}) of the DASB probe and the extent of C=C conversion for an unsaturated polyester formulation (E711 resin, from Owens Corning Fiberglass) with a visible initiator system consisting of 5,7-diiodo-3-6-fluorone (DIBF), 4-octyloxyphenyliodonium hexafluoroantimonate (OPPI) and N,N'-dimethylamino-2,6-diisopropylaniline (DIDMA) with a molar ratio of DIBF/OPPI/DIDMA = 1/2/3. The concentration of DIBF is 0.01 wt%.

Fig. 8. Linear correlation plots between the nascent fluorescence intensity ratio ($I_{coated}/I_{uncoated}$) and the coating thickness for PET bottles coated with DASB probe doped silicone acrylate. ((a) Shoulder Section, (b) Side Section; Probe concentration = 0.015 wt%, Excitation at 302 nm).
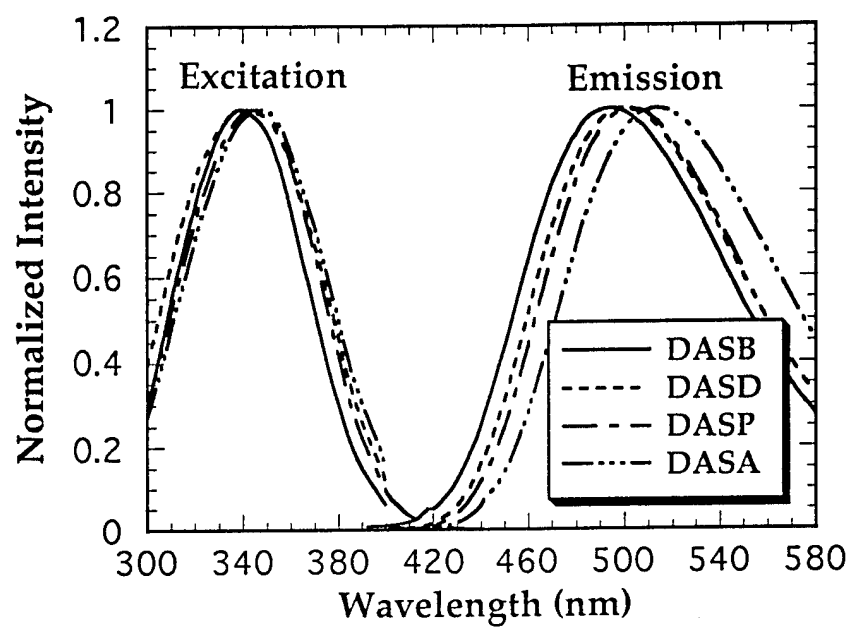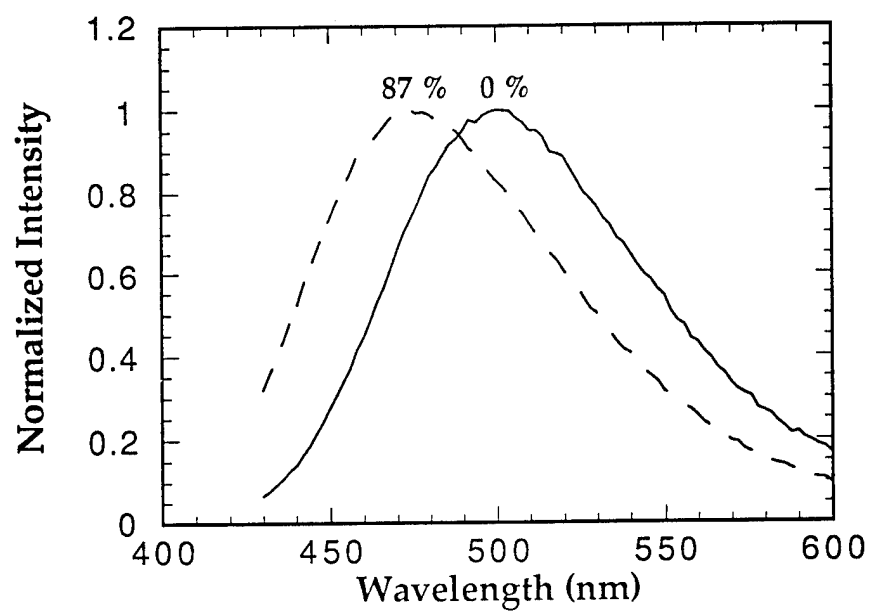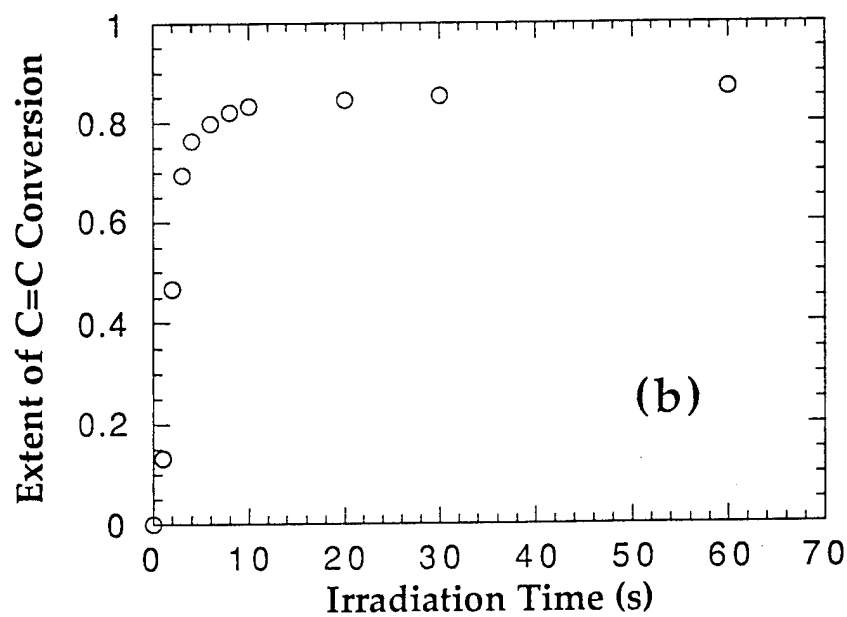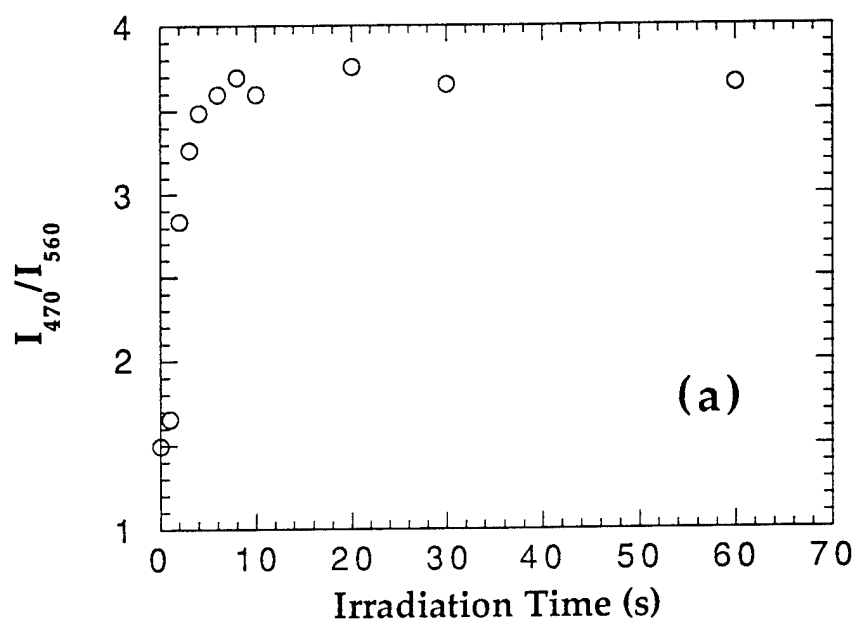
Fig. 1

Fig. 2

Fig. 3
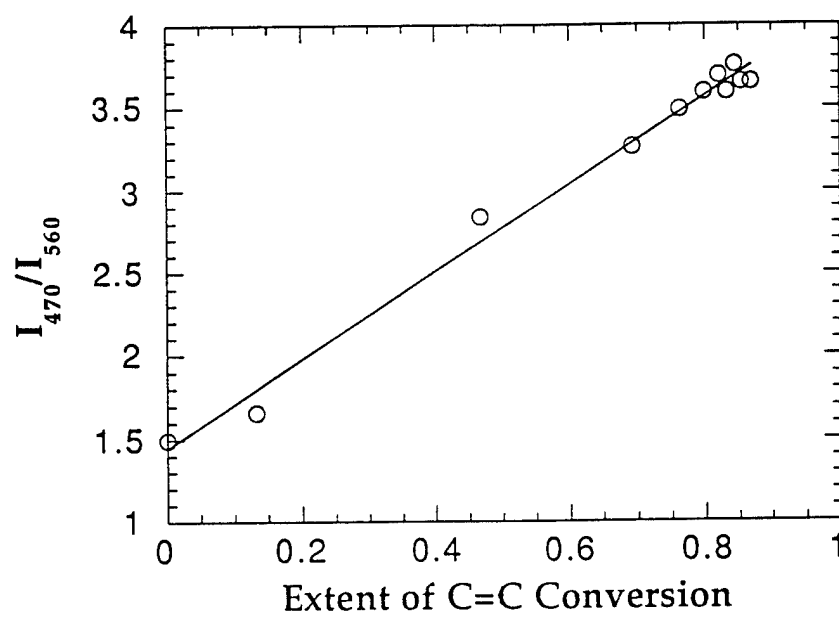
Fig. 4
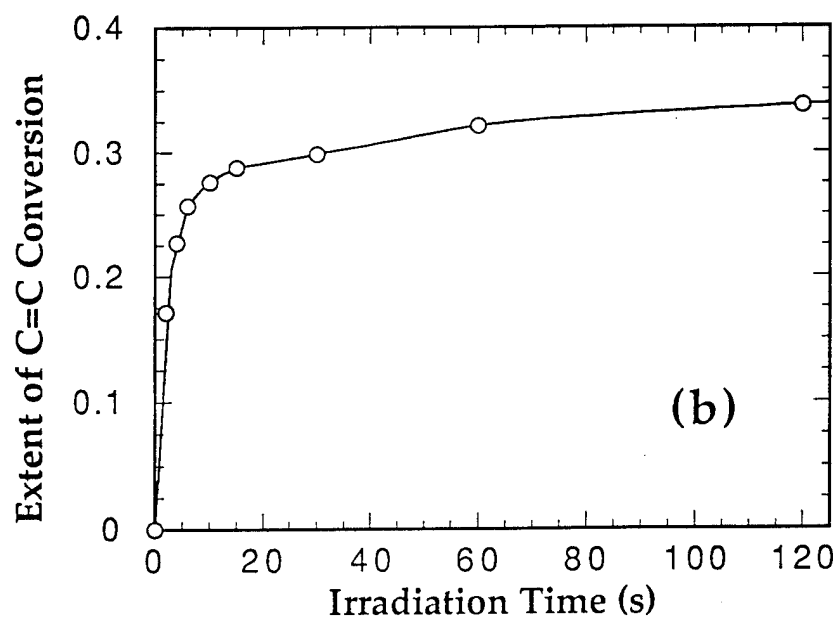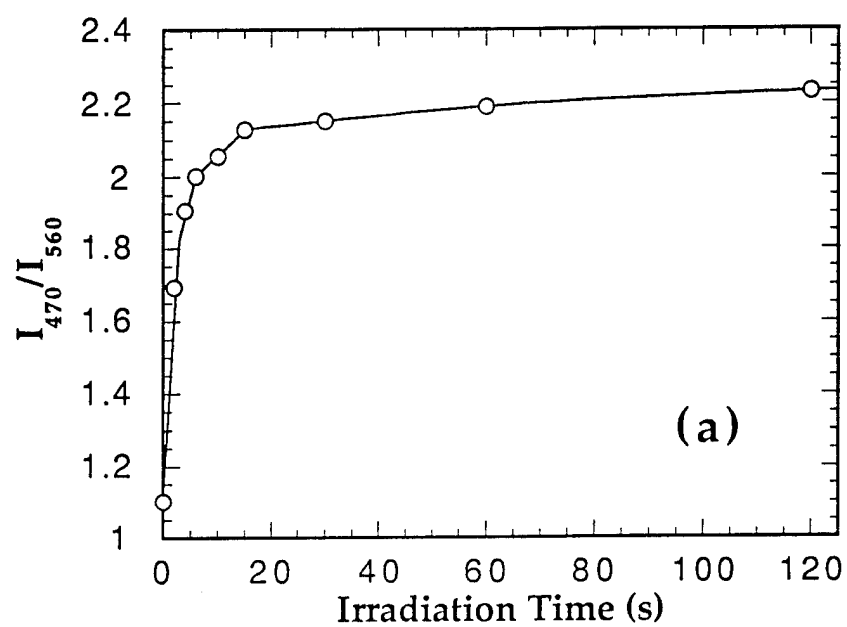
Fig. 5
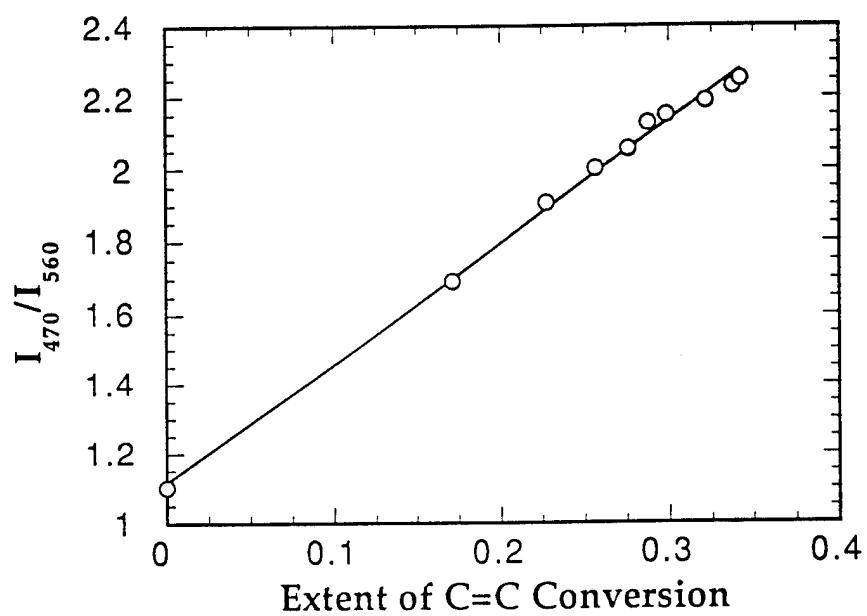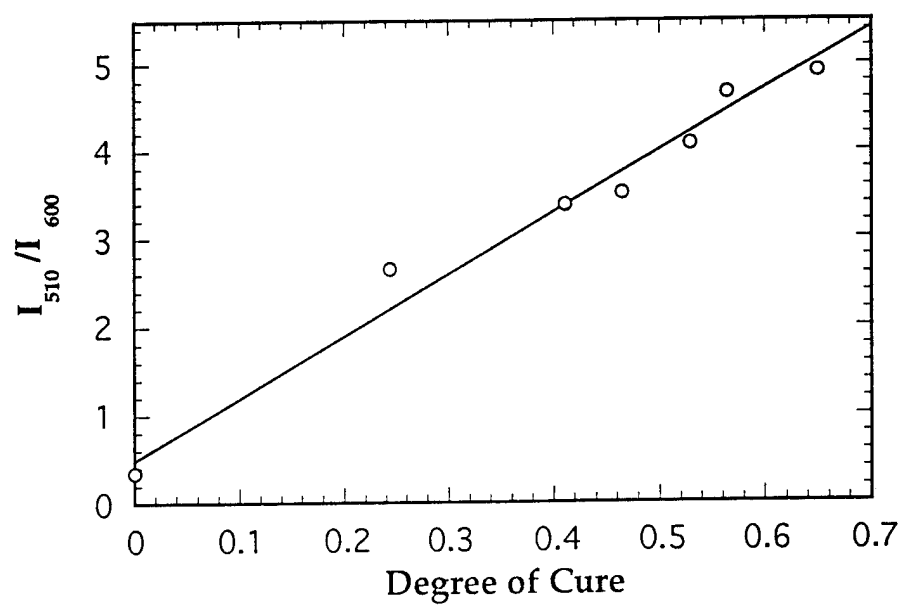
Fig. 6

Fig. 7
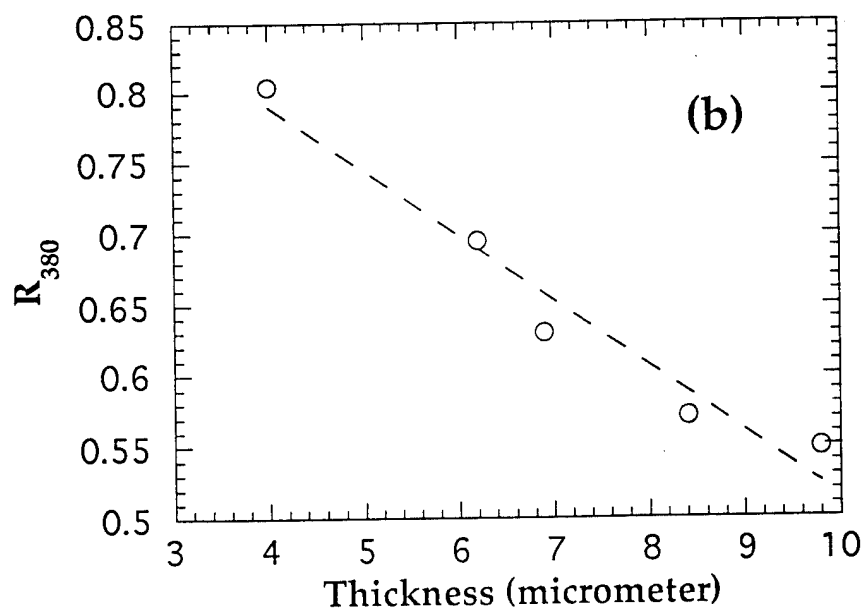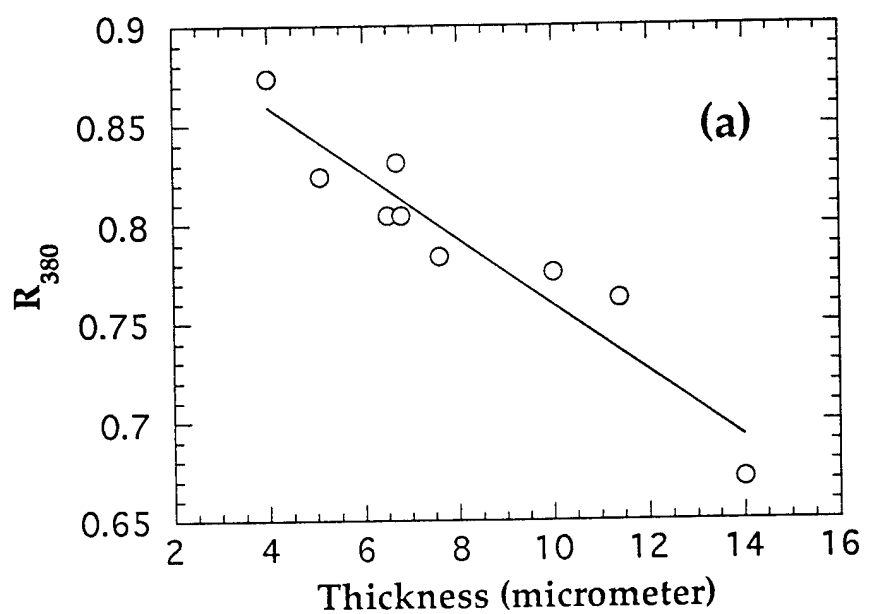
Fig. 8

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