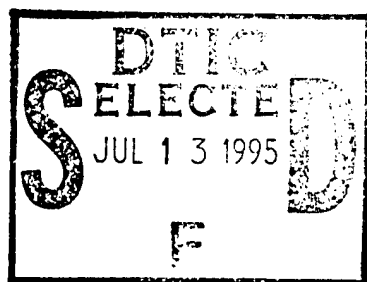OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT: N00014-93-1-0772

R & T Code 313T006

Technical Report #13

Characterization of Photocurable Coatings Using Fluorescence Probes

Song, J. C.; Neckers, D.C. *Polymer Technology and Engineering* in press

D. C. Neckers
Center for Photochemical Sciences
Dept. of Chemistry
Bowling Green State University
Bowling Green, OHIO 43402

Date Submitted
June 15, 1995

REPORT DOCUMENTATION PAGE

OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 6-15-95	3. REPORT TYPE AND DATES COVERED Technical Report

4. TITLE AND SUBTITLE
Characterization of Photocurable Coatings Using Fluorescence Probes

5. FUNDING NUMBERS
G N00014-93-J-1921
R & T 313T006

6. AUTHOR(S)
D.C. Neckers

Kenneth Wynne

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Center for Photochemical Sciences
Bowling Green State University
Bowling Green, Ohio   43402

8. PERFORMING ORGANIZATION REPORT NUMBER

13

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Department of the Navy
Office of Naval Research
800 North Quincy Street
Arlington, VA   22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Song, J. C.; Neckers, D.C. *Polymer Technology and Engineering* in press.

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Reproduction in whole or in part is permitted for any
purpose of the United States Government. This document has
been approved for public release and sale; its distribution
is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

In this paper, we describe a novel method for monitoring the degree of cure and coating thickness of photocurable resins using intramolecular charge transfer (ICT) fluorescence probes such as 5-dimethylaminonaphthalene-1-sulfonyl-n-butylamide (DASB) and 6-propionyl-2-(dimethylamino)-naphthalene (PRODAN). As the curing reaction proceeded, the fluorescence emission spectra of the ICT probes were found to exhibit hypsochromic spectral shifts due to the increase in matrix microviscosity which made it more difficult for the excited molecule to relax to its twisted charge transfer state. The spectral changes of the probes as a function of the degree of the cure were monitored using a fluorescence intensity ratio method which enabled an internal calibration of fluctuations in lamp intensity and sample thickness. It was found that the ratios of the fluorescence emission intensities at two different wavelengths were correlated linearly with the degree of polymerization for various types of photocurable resins. The coating thickness of photopolymers was measured based upon the nascent fluorescence from the coating substrate by virtue of an emission (from the substrate) and absorption (by the coating) mechanism. The thicker the coating, the less the nascent fluorescence emission that can be observed. So the intensity of the nascent fluorescence from the substrate can be correlated to the coating thickness.

14. SUBJECT TERMS

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

Characterization of Photocurable Coatings Using Fluorescence Probes

J. C. Song and D. C. Neckers (a)

Center for Photochemical Sciences (b)
Bowling Green State University
Bowling Green, Ohio 43403

ABSTRACT

In this paper, we describe a novel method for monitoring the degree of cure and coating thickness of photocurable resins using intramolecular charge transfer (ICT) fluorescence probes such as 5-dimethylaminonaphthalene-1-sulfonyl-n-butylamide (DASB) and 6-propionyl-2-(dimethylamino)-naphthalene (PRODAN). As the curing reaction proceeded, the fluorescence emission spectra of the ICT probes were found to exhibit hypsochromic spectral shifts due to the increase in matrix microviscosity which made it more difficult for the excited molecule to relax to its twisted charge transfer state. The spectral changes of the probes as a function of the degree of the cure were monitored using a fluorescence intensity ratio method which enabled an internal calibration of fluctuations in lamp intensity and sample thickness. It was found that the ratios of the fluorescence emission intensities at two different wavelengths were correlated linearly with the degree of polymerization for different types of acrylic or unsaturated polyester resins using either UV or visible (VIS) initiators. The coating thickness of photopolymers was measured based upon the nascent fluorescence from the coating substrate by virtue of an emission (from the substrate) and absorption (by the coating) mechanism. The thicker the coating, the less the nascent fluorescence emission that can be observed. So the intensity of the nascent fluorescence from the substrate can be correlated to the coating thickness.

INTRODUCTION

Radiation curing technology has now found widespread industrial applications due to its high speed, efficiency and solvent-free nature. Photocurable polymers are used in the formulation of various commercial products such as coatings, adhesives, inks and sealants (1). In all of these applications, a photocuring process is used to convert multifunctional monomers such as acrylics into crosslinked polymer networks. The ultimate chemical and physical properties of these polymeric materials depend on various factors, such as monomer structure, forms of initiation, reaction conditions and the rate and degree of polymerization. Thus, a thorough understanding of the photocuring process is essential for property control and processing optimization of the final products.

Characterization of the crosslinked polymer networks is still a challenging task although significant progress has been made. Several methods have been developed to study the kinetics of photopolymerization. Among them are photo-differential scanning calorimetry (PDSC) (2-5), laser interferometry (6), photoacoustic spectroscopy (7), and UV and FTIR spectroscopy (8-10). PDSC is basically like a modified DSC, with a Hg lamp source mounted next to the sample. It has been extensively used to study the kinetics of photopolymerization and the degree of cure can also be measured. However, PDSC is not useful for real time cure monitoring and non-destructive analysis of photopolymers. FTIR is widely used to determine the degree of photopolymerization by monitoring the concentration of residual monomers present in various polymer systems. A real time infra-red (RTIR) technique developed by Decker et al (8-9). allows one to monitor the polymerization process continuously and rapidly in real time. 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). Besides that, transmission IR techniques cannot be used to monitor the degree of polymerization of coatings on opaque

substrates. Also, they are not useful for monitoring polymerization of bulk materials, such as parts made by stereolithography (11).

Fluorescence spectroscopy has gained considerable interest as an analytical tool for polymer cure characterization due to its high sensitivity, selectivity and non-destructive characteristics (12-18). Remote sensing is readily achieved by using fiber-optic cables to transmit optical signals to and from a polymerization system in real time. Recently, Neckers et al. (13-16) reported the successful use of fluorescence probes to monitor the photo-curing process of polyolacrylate monomers. Two types of fluorescence probes were found to be particularly useful. The first were based on "excimer" (i.e. excited dimer) forming molecules, such as pyrene or its derivatives (17). The ratio of the emission intensities of the monomer and excimer was found to correlate well with the degree of cure. The second were based on intramolecular charge transfer molecules, such as 4-(N, N-dimethylamino)benzonitrile (DMABN), and dansyl amide and its derivatives. DMABN exhibits dual fluorescence corresponding to two different singlet excited states (18). The short wavelength (b*) band is due to a coplanar (parallel) excited state conformation while the long wavelength (a*) band originates from a perpendicular conformation which is the so-called twisted intramolecular charge transfer (TICT) state. The coplanar conformation is more stable in the ground state because of a higher degree of delocalization of the π orbitals. Therefore, the coplanar excited state will be directly populated from the ground state. However, the perpendicular excited state is energetically more stable due to a large charge separation. This implies that the molecules are first excited to the b* conformation and then "cross" or relax to the a* conformation, making the population of the perpendicular conformation strongly dependent upon the microenvironment of the TICT molecule. In fact, fluorescence spectra of TICT probes were found to be very sensitive to changes in the microviscosity of the medium (13-16). In particular, the ratio of the emission intensities at two different emission wavelengths can be correlated linearly with the degree of cure for various polyolacrylate monomer systems.

In this paper, we present the results of our recent study on using 5-dimethylaminonaphthalene-1-sulfonyl-n-butylamide (DASB) and 6-propionyl-2-(dimethylamino)naphthalene (PRODAN) (see Chart I) as fluorescence probes for characterization of a variety of photopolymerized acrylic and unsaturated polyester resins obtained, mainly, from commercial suppliers. The resin systems were chosen as representatives of diverse applications in the photo cure industry. Our results indicate the technique to be both versatile and generally applicable in a variety of photocurable systems.

EXPERIMENTAL SECTION

Materials. 5-Dimethylaminonaphthalene-1-sulfonyl-n-butylamide (DASB) was synthesized from the reaction of 5-dimethylaminonaphthalene-1-sulfonyl chloride (DASC) with an excess of n-butylamine in THF. In a typical procedure, 2.7 g (0.01 mole) DASC (Kodak) was first dissolved in 20 ml anhydrous THF and 5 ml n-butylamine was added. After stirring at room temperature overnight, the reaction mixture was taken to dryness using a rotavapor. The residue was then dissolved in 20 ml dichloromethane and 20 ml distilled water was added with a few drops of concentrated HCl. The organic phase containing the product was then extracted and dried. The residue was dissolved in a little ethanol and on addition of water, DASB crystallized. The product was recrystallized from ethanol-water (50/50 vol.%. ^{1}H-NMR (CDCl$_3$), δ, ppm: 0.75 (3H, t, J=7.2Hz), 1.11-1.42 (4H, m), 2.83-2.93 (8H, overlapping s, m), 4.55 (1H, t, J=6.3 Hz), 7.19 (1H, d, J=7.4 Hz), 7.55 (2H, m), 8.27 (2H, m), 8.55 (1H, d, J=8.6 Hz). m.p. = 92°C, mass spectrum m/e = 306.

6-Propionyl-2-dimethylaminonaphthalene (PRODAN) was purchased from Molecular Probes, Inc. and used without further purification.

A mixture of multifunctional acrylates was made by mixing polyethylene glycol-400 diacrylate, PEGA-400 (Monomer-Polymer and Dajac Labs, Inc.), trimethylolpropane triacrylate, TMPTA (Saret 351, from the Sartomer Co.), and

dipentaerythrytol monohydroxy pentaacrylate, DPHPA (Sartomer 399, from the Sartomer Chemical Co.), in a weight percentage ratio of 20/40/40, respectively. A fluorone dye, 5,7-diiodo-3-butoxy-6-fluorone, DIBF, developed in our group (21), was utilized as the visible (VIS) initiator at a concentration of about 5×10^{-4} M. Amine coinitiators, either N-phenyl glycine, NPG (Aldrich) or N,N'-dimethylamino-2,6-diisopropylaniline, DIDMA (Aldrich), were used at a concentration of about 5×10^{-2} M. The coinitiator in this case acts as an electron donor to the excited state of the dye, before the generation of free radicals (21).

To photocure commercial unsaturated polyester or polyester acrylate resins, 5,7-diiodo-3-butoxy-6-fluorone (DIBF) was utilized as the visible initiator at a concentration of 0.10 or 0.15 wt%. The coinitiator system was composed of an onium salt, 4-octyloxylphenyliodonium hexafluoroantimonate (OPPI), and an amine, N,N'-dimethylamino-2,6-diisopropylaniline, (DIDMA). The molar ratio of DIBF/OPPI/DIDMA is 1/2/3. A typical formulation of the photocurable system consists 10 g of an as-received resin, 10 mg DIBF, 24.8 mg OPPI, 11.8 mg DIDMA and 1.0 mg DASB. The mixture was mixed thoroughly before the photocuring process.

Several types of commercial UV-curable acrylated coatings were investigated. These included two fiber optic coating formulations including a primary coating (Desotech 950-076, from DSM) and a secondary coating (Desolite 950-044, from DSM); a polyester acrylate floor coating formulation (Duracote, from Armstrong World Industries); two acrylic coating formulations for vinyl sheets (Durethane R602Z70 and R509Z70, from PPG Industries), a silicone acrylate (UV8550-D1, from GE Silicones) and an unsaturated polyester resin (from Owens-Corning Fiberglass). The fluorescence probe, DASB or PRODAN was mixed into the photocurable monomer solutions to be studied at a concentration of about $1-5 \times 10^{-4}$ M/L.

Cure Monitoring Procedure

The photocuring process was carried out using either a medium pressure Hg arc lamp or a 75 W Tungsten-Halogen bulb. The degree of polymerization for different samples was varied by changing the exposure time. A few drops of monomer solution being studied were first squeezed between two pieces of glass slides (or NaCl plates for IR measurements) with spacers of appropriate thicknesses at the edges to control the final thickness. Steady state fluorescence emission spectra of samples cured for different periods of time were obtained via a Spex Fluorolog-2 spectrophotometer. Remote measurement was carried out using a bifurcated fiber-optic cable attached to the excitation and emission monochromators, respectively.

Infra-red measurement of the extent of double bond conversion was accomplished using a Mattson Galaxy Series 6020 FT-IR spectrometer with a spectral resolution of 2 cm^{-1}. The extent of C=C conversion (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.

Differential Scanning Calorimetry (DSC) analysis was accomplished using a Perkin-Elmer DSC-4 thermal analyzer with a Model 3600 data station. The heat of reactions of resin samples (15-20 mg) photocured for various periods of times were determined by dynamic DSC scanning (heating rate = 20 °C) using stainless steel pans under a constant purging of dry N_2. The degree of cure (α) was calculated using the following equation.

$$\alpha = 1- \Delta H_{residue}/\Delta H_{total} \qquad (2)$$

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.

RESULTS AND DISCUSSION

Fluorescence Probe Study

It is known that aromatic amines possessing a strong donor and acceptor substituent often exhibit intramolecular charge transfer properties with a large Stokes shift or dual fluorescence. 5-Dimethylaminonaphthalene-1-sulfonyl-n-butylamide (DASB) is a highly fluorescing compound with a large Stokes shift (152 nm in THF). Fig. 1 shows the fluorescence excitation and emission spectra of DASB in THF. The excitation and emission maxima were found to be at 342 and 494 nm, respectively. Its fluorescence quantum yield (Φ_f) was measured to be about 0.5 in THF solution using 9,10-diphenylanthracene as the standard. These distinct fluorescence characteristics of DASB have been employed to detect trace amounts of amines and amino acids in liquid chromatography (22). Okamoto et al (23) reported a kinetic study on the reaction of fluorescent reagent, 5-dimethylaminonaphthalene-1-sulphonyl chloride (DASC) with n-butyl amines by monitoring the fluorescence emission of the product, DASB, in various nonaqueous solvents. The reaction was found to proceed quantitatively by simple second-order kinetics with rate constants of the order 10^{-3} to 10^{-1} $M^{-1}s^{-1}$ at the temperature of 30 to 50 °C. For polymer cure monitoring applications, the high fluorescence quantum yield and large Stokes shift of the DASB probe is advantageous. Since spectral blue shifts in the ICT probe fluorescence emission are often observed as the matrix viscosity increases during a curing process, a larger separation between the absorption and emission peaks offer a wider spectrum window and the intrinsic fluorescence from the photopolymer (if any) would be less prone to interfere with the probe fluorescence signals.

PRODAN, 6-propionyl-2-(dimethylamino)naphthalene, was first synthesized by Weber and Farris as a hydrophobic fluorescence probe (24). Its fluorescence emission spectrum exhibits a remarkably large red-shift as the solvent polarity increases, due to the formation of charge transfer (CT) state in polar solvents. Studies of the pressure effects on the fluorescence properties of PRODAN by Rollinson and Drickamer (25) showed that the shorter wavelength fluorescence in non-polar media was attributed to a locally excited (LE) state and the longer wavelength fluorescence in polar media due to the formation of a twisted excited conformer. Heisel, et al. (26) studied the fluorescence decays and the time-resolved spectra of PRODAN in n-butanol at low temperatures and confirmed the existence of an energetically lower charge transfer excited state due to polar solute-solvent interactions. It was found that the fluorescence emission peak position of PRODAN in n-butanol shifted to shorter wavelengths on decreasing the temperature. This indicates that the fluorescence peak position of PRODAN is viscosity dependent. As the matrix viscosity increases, the difficulty for an excited PRODAN molecule to relax to its lowest charge transfer state increases, thus leading to a blue shift in the fluorescence emission spectra.

Fig. 2 compares the fluorescence emission spectra (λ_{ex} = 380 nm) of DASB in a commercial acrylate coating formulation (Desotech 950-076, used as a primary coating for fibers) before (0% C=C conversion) and after curing for 30 sec (~95% C=C conversion) using a medium pressure H_g lamp. A total spectral blue shift of ~ 20 nm was obtained. This spectral blue shift was due to increases in the medium viscosity which makes it more difficult to form the long wavelength twisted conformation in the excited state. A total spectral blue shift of about 14 nm was observed when PRODAN was used as the fluorescence probe in the same resin formulation. To follow the changes in the probe emission spectra, we used a fluorescence intensity ratio method in which fluorescence intensity values at two different wavelengths (R = $I_{||}/I_{\perp}$) were monitored. $I_{||}$ and $I_{\perp}$ represent the fluorescence emission intensity values corresponding to the parallel and

perpendicular conformations, respectively, in the excited states of the probe. The ratio method produces an internal calibration for any changes in sample thickness and lamp intensity during the cure monitoring process. Linear correlations between the extent of double bond conversion vs. the probe fluorescence intensity ratio were obtained when both probes were used to monitor the photocuring process of acrylic fiber coating, as shown in Fig. 3. However, DASB is advantageous because it is less expensive than PRODAN.

Cure Monitoring of UV-Curable Acrylic Coatings

(1) Acrylic Coatings for Optical Fibers. UV curable acrylic coatings are applied to optical fibers for protection purposes. Generally, two types of coatings are used: a primary coating usually with a more flexible and soft structure such as those of aliphatic urethane acrylates; and a harder secondary coating containing photocurable acrylic monomers like aromatic epoxy acrylates to provide the necessary mechanical strength. Fig. 4 compares the changes in the extent of double bond conversion as a function of irradiation time under a medium pressure Hg lamp for the two fiber coating formulations studied. We can see that the initial cure rate of the primary coating is significantly slower than that of the secondary coating. An induction time of about two seconds was observed for the primary coating while that of secondary coating was less than one tenth of a second. However, the overall extent of cure of the primary coating (~95 %) was much higher than that of secondary coating (~60 %). This is probably due to the difference in cure rate. A faster cure rate in the secondary coating formulation can result in a rapid increase in the crosslinking density which in turn makes it difficult for the propagating radicals to diffuse to the unreacted acrylate functional groups to continue the polymerization process, thus a lower extent of cure is observed. Results of the fluorescence probe (DASB) studies of the photocuring processes of the two coating formulations correlates well with the FTIR results. The probe fluorescence ratio, $R = I_{470}/I_{560}$, increases linearly with the extent of double bond conversion for the both fiber coating formulations as shown in Fig. 5.

Therefore, the DASB probe can be used to monitor the photocuring processes of acrylic coatings for optical fibers.

(2). Acrylic coatings for plastics. UV curable acrylic resins are widely used as coatings on plastic materials such as polystyrene, polyvinyl chloride (PVC) and polyethylene terephthalate (PET). To demonstrate the applicability of the fluorescent probe technique, we doped the DASB probe into two types of acrylic coating formulations: an alpha gloss Durethane coating (from the PPG Industries) and a low gloss coating also from the PPG. The Durethane coating formulations contain mainly 2-ethylhexyl acrylate monomer with a UV initiator (benzophenone/amine). DASB was readily dissolved into both coating formulations at a concentration of 0.016 wt% before the photocuring process. Fig. 6 compares the fluorescence and FTIR cure monitoring profiles of the alpha gloss Durethane resin as a function of the irradiation time using a medium pressure mercury lamp. It can be seen that the two cure profiles are very similar as the probe fluorescence ratio increases from ~ 1.5 (0 % C=C conversion) to ~ 3.7 (~90% C=C conversion) after photocuring for 60 sec. Fig. 7a demonstrates a linear correlation between the probe fluorescence ratio (I_{470}/I_{560}) and the extent of C=C conversion. Although the low gloss UV curable coating formulation was found to have a faster cure rate than the alpha gloss coating formulation, a linear correlation curve between the fluorescence probe response (I_{470}/I_{560}) and the extent of C=C conversion was obtained as shown in Fig. 7b.

Silicone acrylate is another important class of photocurable resin for coating applications. In a similar manner, we examined the applicability of the DASB probe for cure monitoring of a commercial UV-curable silicone acrylate resin obtained from GE Silicones. The fluorescence ratio (I_{470}/I_{560}) was found to increase from ~ 1.4 (0% C=C conversion) to ~ 4.8 (68 % C=C conversion) after curing for about 5 min. under a medium pressure mercury lamp. A linear correlation curve between the fluorescence ratio (I_{470}/I_{560}) and the extent of double bond conversion was obtained

as shown in Fig. 8. It is noted that the total change in fluorescence ratio of the silicone acrylate resin before and after curing is significantly larger than other UV curable resins (Table 1). These differences in the slopes of the correlation curves may reflect some useful structural information such as the crosslinking density of photopolymerized acrylated polymer networks. An ICT probe in a high crosslinking density polymer matrix is expected to give a larger value of the fluorescence intensity ratio than that in a low crosslinking density polymer matrix, even though their degrees of polymerization are the same. Future work in this area will certainly lead to some interesting findings.

(3). Photopolymerization using fluorone dye visible initiators. Visible initiators such as fluorone dye/coinitiator systems developed in our laboratories have been successfully used for both free radical (27) and cationic (28) photopolymerization processes. Because these initiators bleach as they initiate polymerization, a large cure depth can be obtained. However, the fluorone dyes may exhibit fluorescence emission in photopolymers after a low degree of polymerization and an incomplete photobleaching of the photoinitiators. It is interesting to know the effects of visible initiators on the fluorescence spectra of the DASB probe. Thus we investigated the applicability of the new fluorescence probe to monitor the photocuring reaction of multifunctional acrylates initiated via the visible dye initiators developed in our laboratories (21). The monomer solution was a typical formulation used in our stereolithographic applications: a mixture of multifunctional acrylate monomers including TMPTA, DPHPA, polyethylene glycol diacrylate with a fluorone dye initiator (DIBF) and an amine coinitiator (NPG). The fluorescence emission intensity ratio (I_{470}/I_{560}) of the DASB probe was found to increase linearly from 1.1 (0% conversion) to about 2.2 (32% conversion) as shown in Fig. 9a.

DASB was also used to monitor the photocuring process of a commercial polyester acrylate resin used in floor coating applications. For photoinitiation, a "hybrid" initiating system containing a fluorone dye initiator (DIBF), an onium salt

(4-octyloxylphenyliodonium hexafluoro antimonate, OPPI) and an amine (DIDMA) was used (28). The incorporation of the onium salt in the initiating system produces a synergistic effect during the photoinitiation process which enables a satisfactory cure while significantly reducing the amount of DIDMA coinitiator used in the formulation (29). It was found the fluorescence intensity of the DASB probe decreased significantly when OPPI was introduced into the initiator formulation, especially in the early stage of the photocuring. This is probably due to the quenching effect by the acid generated during the irradiation of the onium salt. Nevertheless, a linear correlation between the fluorescence intensity ratio (I_{470}/I_{560}) and the extent of C=C conversion was obtained for a polyester acrylate resin system cured with DIBF/OPPI/DIDMA (1/2/3, molar ratio, DIBF = 0.1 wt%), as shown in Fig. 9b.

More recently, we investigated the applicabilities of the fluorescence probe technique for cure monitoring of unsaturated polyester resins using visible initiator systems. The commercial resin system studied is from the Owens-Corning Fiberglass Corporation and is a mixture of unsaturated polyester and styrene. The fluorescence probe, 5-dimethylaminonaphthalene-1-sulphonyl-n-butylamide (DASB) was readily dissolved into the resin formulation at a concentration of 0.01 wt% before the photocuring process. As the curing reaction proceeded, the probe fluorescence emission peak position shifted from 536 to 498 nm (a total spectral blue shift of 38 nm) as the degree of cure increased from 0% to ~ 70 %. Because of the problem of peak overlapping in the infra-red spectra, it was difficult to use FTIR to monitor the degree of cure of this unsaturated polyester formulation. Thus DSC was used to determine the degree of cure by comparing the residual heat of reaction with the total heat reaction obtained when 1 wt.% benzoyl peroxide was used as the thermal initiator. The DSC results correlate very well with the fluorescence intensity ratios (I_{470}/I_{560}) as shown in Fig. 10. Thus, it is demonstrated that fluorescence probe response can correlate with both FTIR and DSC techniques. Since the intramolecular charge transfer probes are sensitive to the changes in microviscosity, we can also

correlate the probe fluorescence response with other physical/mechanical properties such as glass transition temperature (Tg), modulus, hardness and strength of a polymer network.

3. Fluorescence Probe Depth (τ_p) Estimation

According to the definition of fluorescence quantum yield (Φ_f),

$$\Phi_f = I_f/I_a \tag{3}$$

fluorescence intensity (I_f) is proportional to the amount of light absorbed (I_a).

$$I_f = \Phi_f {*} I_a \tag{4}$$

$$I_a = I_0 - I_t \tag{5}$$

$$I_a = I_0(1-e^{-2.303\varepsilon c\tau}) \tag{6}$$

where I_0 and I_t are the intensity values of the incidence and transmitted light, respectively; ε is the molar absorptivity, c is the concentration of the probe and τ is the thickness of the sample probed.

$$I_f = \Phi_f I_0 (1-e^{-2.303\varepsilon c\tau}) \tag{7}$$

$$\delta I_f/\delta\tau = 2.303\Phi_f I_0 \varepsilon c\, e^{-2.303\varepsilon c\tau} \tag{8}$$

At the surface of the sample, $\tau = 0$, then

$$\delta I_f/\delta\tau\, |_{\tau = 0} = 2.303\Phi_f I_0 \varepsilon c \tag{9}$$

If the probe depth (τ_p) is defined as the thickness when $\delta I_f/\delta\tau$ (τ) decreases to one tenth of its value at the surface, then

$$\delta I_f/\delta\tau\, |_{\tau = \tau_p} = 2.303\Phi_f I_0 \varepsilon c\, e^{-2.303\varepsilon c\tau_p}$$

$$= 2.303\Phi_f I_0 \varepsilon c/10 \tag{10}$$

Thus $\qquad \tau_p = 1/\varepsilon c \tag{11}$

Therefore, the probe depth is inversely proportional to the absorption coefficient and the concentration of the probe. This is to be expected as the more the absorbance, the less the penetration depth of the excitation light. Control of the probe depth can be achieved by adjusting the probe concentration and/or the excitation wavelength since ε is wavelength dependent. It must be pointed out that Eq. 11 is only good for clear coating cases in which there is no absorption due to

other components in the photopolymer system besides the probe. For DASB, if used at a concentration of 5×10^{-4} M/L, the probe depth is estimated to be 3 to 30 mm in a clear coating system. In practice, however, commercial photocurable coating formulations and especially pigmented systems are not completely transparent at the probe excitation wavelength region and probe depths shorter than what is predicted by using Eq. 11 are expected.

4. Coating Thickness Measurement

Coating thickness is another important parameter that requires to be constantly monitored and controlled in the coating industry in order to achieve a uniform coating. However on-line and nondestructive measurement of coating thickness is still a challenging task. Because of its high sensitivity and nondestructive characteristics, we expected the fluorescence probe technique would be useful in this regard. The idea was to utilize the nascent fluorescence from the coating substrate and quench it via absorption of the emission. By doping a fluorescence probe that can absorb the nascent fluorescence from the substrate, the thicker the applied coating, the less the fluorescence emission signals can be detected from the substrate. Thus the nascent fluorescence intensity is expected to be inversely proportional to the coating thickness. Most coating substrates such as plastics, wood, glass and paper exhibit fluorescence emissions when irradiated by a UV light, thus enabling the measurement of the coating thickness.

Fig. 11 shows the nascent fluorescence excitation and emission spectra of the polyethylene terephthalate (PET) materials used in a number of applications. The peak positions for the excitation and emission spectra are at 345 and 384 nm, respectively, for the samples measured. When a coating solution containing UV curable silicone acrylate and fluorescence probe (DASB, C=0.0005 M/L) was applied to the PET substrate, the nascent fluorescence intensity at 380 nm was found to decrease as the coating thickness increased as shown in Fig. 12. The excitation wavelength was chosen as 302 nm which gives the most sensitive measurement.

Fig. 13 shows a linear correlation curve between the reduced fluorescence intensity at 380 nm (ratio of the fluorescence intensity of the coated vs. the noncoated substrate) and the coating thickness.

SUMMARY

Intramolecular charge transfer (ICT) fluorescence probes such as 5-dimethylamino-naphthalene-1-sulfonyl-n-butylamide (DASB) and 6-propionyl-2-(dimethylamino)-naphthalene (PRODAN) are useful for cure monitoring of photocurable acrylic systems with UV or visible initiators. As the curing proceeds, the fluorescence emission spectra of the probes exhibited hypsochromic spectral shifts due to the increases in matrix microviscosity. Linear correlations between the fluorescence intensity ratios and the extent of polymerization were obtained. With a fiber-optic fluorimeter, this fluorescence cure sensing technique based on ICT fluorescence probes can be readily applied to photopolymerized films, coatings and bulk materials. The technique can be applied in a variety of commercial photocurable resins.

REFERENCES

1. C.E. Hoyle, in _Radiation Curing of Polymeric Materials;_ C.E. Hoyle, J. F. Kinstle, eds.; ACS Symposium Series 417; American Chemical Society, Washington, DC, (1990), Chapter 1, p1.

2. G.R. Tyson and A.R. Shultz, _J. Polym. Sci., Polym. Chem. Ed._, 17, 2059 (1979).

3. W.D. Cook, _Polymer_, 33, 2152 (1992).

4. D. Wang, L. Carrera, and M.J.M. Aradie, _Eur. Polym. J._, 29, 1379 (1993).

5. C.E. Hoyle, R.D. Hensel and M. B. Grubb, _J. Polym. Sci., Polym. Chem. Ed._, 22, 1865 (1984).

6. J.E. Moore, _UV Curing: Science and Technology_, Technology Marketing Corporation, (1978).

7. R.D. Small, J.A. Ors and B.S. Royse, _ACS Symp. Series # 242_, 325 (1984).

8. C. Decker and K. Moussa, _ACS Symp. Series # 417_, 439 (1990).

9. C. Decker, _J. Polym. Sci. Part A: Polym. Chem._, 30, 913 (1992).

10. N.S. Allen, S.J. Hardy, A.F. Jacobine, D.M. Glaser, B. Yang and D. Wolf, _Eur. Polym. J._, 26, 1041 (1990).

11. D.C. Neckers, _Chemtech_, 20, 615 (1990).

12. J.C. Song and C.S.P. Sung, _Macromolecules_, 26, 4818 (1993), and references therein.

13. J. Paczkowski and D. C. Neckers, _Macromolecules_, 25, 548 (1992).

14. X. Zhang, I. N. Kotchetov, J. Paczkowski and D. C. Neckers, _J. Imaging Sci. Tech._, 36, 322 (1992).

15. I. N. Kotchetov and D. C. Neckers, _J. Imaging Sci. Tech._, 37, 156 (1993).

16. J. Paczkowski and D. C. Neckers, _J. Polym. Sci., Polym. Chem. Ed._, 31, 841 (1993).

17. O. Valdes-Aguilera, C.P. Pathak and D.C. Neckers, _Macromolecules_, 23, 689 (1990).

18. J. Lipinski, H. Chojnacki, R. Rotkiewicz and Z.R. Grabowski, _Chem. Phys. Lett._, 70, 449 (1980).

19. D. C. Neckers and T. Tanabe, unpublished.

20. (a). G. Mellbin and B.E.F. Smith, _J. Chrom._, 312, 203 (1984); (b). P. Lehtonen, _J. Chrom._, 314, 141 (1984); (c). _ibid._, 330, 243 (1985).

21. A. Okamoto, U. Katsumi and I. Mita, _Bull. Chem. Soc. Jpn._, 55, 3068 (1982).

22. G. Weber and F. J. Farris, _Biochemistry_, 18, 3075 (1979).

23. A.M. Rollinson and H.G. Drickamer, _J. Chem. Phys._, 73, 5981 (1980).

24. F. Heisel, J.A. Miehe and A.W. Szemik, _Chem. Phys. Letts._, 138, 321 (1987).

25. (a) O. Valdes-Aguilera, C.P. Pathak, J. Shi, D. Watson and D.C. Neckers, _Macromolecules_, 25, 541 (1992). (b) A. Torres-Filho and D.C. Neckers, _J. Appl. Polym. Sci._, 51, 931 (1994). (c) A. Torres-Filho and D.C. Neckers, _RadTech Conf. Proc._, 1, 259 (1994).

26. (a) Y. Bi and D.C. Neckers, _Macromolecules_, 27, 3683 (1994). (b) Y. Bi and D.C. Neckers, _RadTech Conf. Proc._, 1, 180 (1994).

27.   T. Marino, D. Martin and D.C. Neckers, *RadTech Conf. Proc.*, **1,** 169 (1994).

Table 1. <u>Slopes and intercepts of the correlation curves between the probe fluorescence intensity ratio and the degree of cure for different photocurable resins using DASB as the fluorescence probe</u>

Resin System	Intercept	Slope
Acrylic Coating for Fibers (Primary)[1]	1.38	2.63
Acrylic Coating for Fibers (Secondary)[2]	1.63	2.32
Acrylic Coating for Vinyls (Alpha Gloss)[3]	1.45	2.65
Acrylic Coating for Vinyls (Low Gloss)[4]	1.24	2.71
Silicone Acrylate[5]	1.34	4.82
Multifunctional Acrylate[6]	1.12	3.39
Polyester Acrylate[7]	0.902	2.75
Unsaturated Polyester[8]	0.0043	0.475

Notes: 1. A UV curable acrylic formulation (Desotech 950-076) from DSM Desotech Inc., Elgin, Illinois.

2. A UV curable acrylic formulation (Desolite 950-044) from DSM

Desotech Inc., Elgin, Illinois.

3. A UV curable acrylic formulation (Alpha gloss Durethane) from PPG Industries, Inc., Allison Park, PA.

4. A UV curable acrylic formulation (Low gloss Durethane) from PPG Industries, Inc., Allison Park, PA.

5. A UV curable silicone acrylic formulation from GE Silicones, Waterford, NY.

6. This polyester acrylate coating (Duracoat) is from the Armstrong World Ind., Lancaster, PA. The visible initiator system used consists 5,7-diiodo-3-butoxy-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%.

7. The multifunctional acrylate mixture was made of 20 wt% of polyethylene glycol-400-diacrylate (PEGA), 40 wt% of trimethylolpropane triacrylate (TMPTA) and 40 wt% dipentaerythrytol monohydroxy pentaacrylate (DPHPA). The visible initiator used is DIBF (5×10^{-4} molar) with N-phenyl glycine (NPG, 5×10^{-2} molar) as the coinitiator.

8. A mixture of unsaturated polyesters and styrene from Owens-Corning Fiberglass, Research and Development Center, Granville, OH. The visible initiator system consists 5,7-diiodo-3-butoxy-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%.

Figure Captions

Figure 1.   Fluorescence excitation and emission spectra of 5-dimethylamino-naphthalene-1-sulfonyl-n-butylamide (DASB) in THF.

Figure 2.   Fluorescence emission spectra of DASB probe in a commercial acrylate coating formulation (Desotech 950-076) as a function of the extent of C=C conversion (Excitation at 380 nm).

Figure 3.   Linear correlation curves between probe fluorescence intensity ratios and the extent of C=C conversion of a commercial acrylic fiber coating using DASB and PRODAN, respectively, as fluorescence probes. (Excitation at 380 nm and 370 nm, respectively, for DASB and PRODAN).

Figure 4.   Changes in the extent of double bond conversion as a function of irradiation time under a medium pressure H_g lamp for the two fiber coating formulations studied.

Figure 5.   Linear correlation curves between probe fluorescence intensity ratio and the extent of C=C conversion for two commercial fiber coating resins: (a). Primary coating; (b). Secondary coating. (DASB probe, Excitation at 380 nm).

Figure 6.   Comparisons of the fluorescence (a) and FTIR (b) cure monitoring profiles of a UV curable resin (from PPG Industries) as a function of irradiation time using a medium pressure mercury lamp.

Figure 7. Linear correlation curves between probe fluorescence intensity ratio and the extent of C=C conversion for two commercial vinyl coating resins: (a). Alpha gloss coating; (b). Low gloss coating. (DASB probe, Excitation at 380 nm).

Figure 8. Linear correlation curves between probe fluorescence intensity ratio and the extent of C=C conversion for a UV curable silicone acrylate resin. (DASB probe, excitation at 380 nm).

Figure 9. Linear correlation curves between probe fluorescence intensity ratio and the extent of C=C conversion for two visible light cured resin systems: (a). A mixture of multifunctional acrylate; (b). Polyester acrylate (Duracoat). (DASB probe, Excitation at 380 nm).

Figure 10. Linear correlation plot between the fluorescence intensity ratios (I_{470}/I_{560}) and the degree of cure for the resin using SGL's 470B visible photoinitiator (DIBF/OPPI/DIDMA = 1/2/3, [DIBF]= 0.10 wt%). (DASB probe, excitation at 380 nm).

Figure 11. Nascent fluorescence excitation and emission spectra of a polyethylene terephthalate (PET) material. (Excitation at 345 nm, Emission at 384 nm).

Figure 12. Changes of PET nascent fluorescence emission spectra as a function of coating thickness of a fluorescence probe doped silicone acrylate resin on a PET plastic substrate. (DASB probe, Excitation at 302 nm).

Figure 13. Correlation plot of the fluorescence intensity ratio ($R380$, $I_{coated}/I_{noncoated}$) vs. the coating thickness for a fluorescence probe doped silicone acrylate resin on a PET plastic substrate. (DASB probe, Excitation at 302 nm).

Chart I. Structures of Fluorescence Probes Studied.
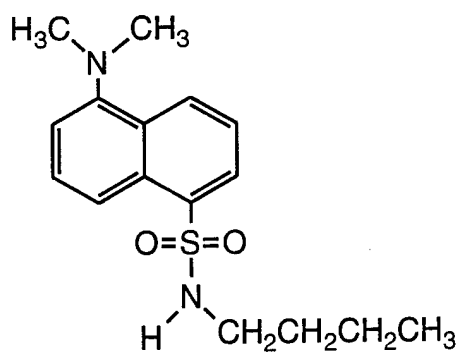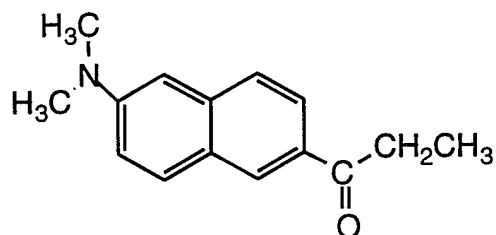
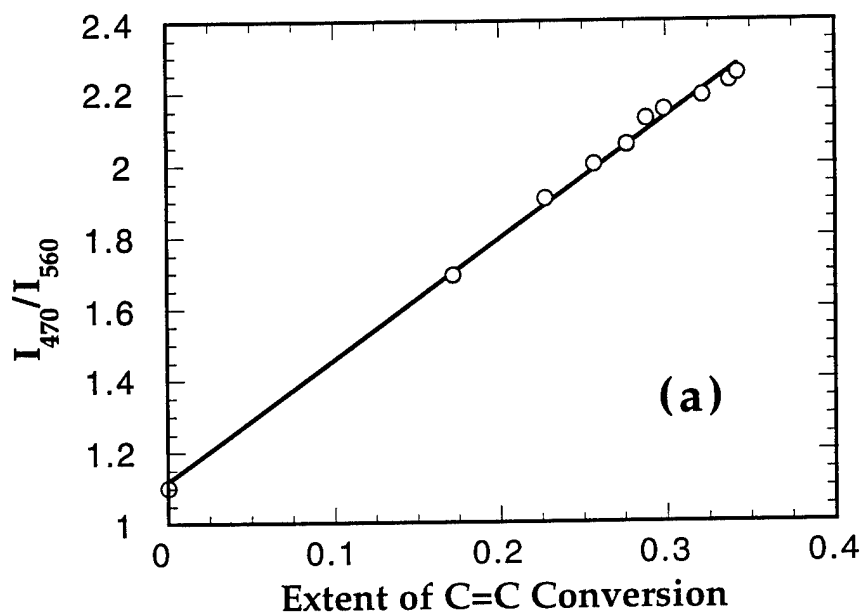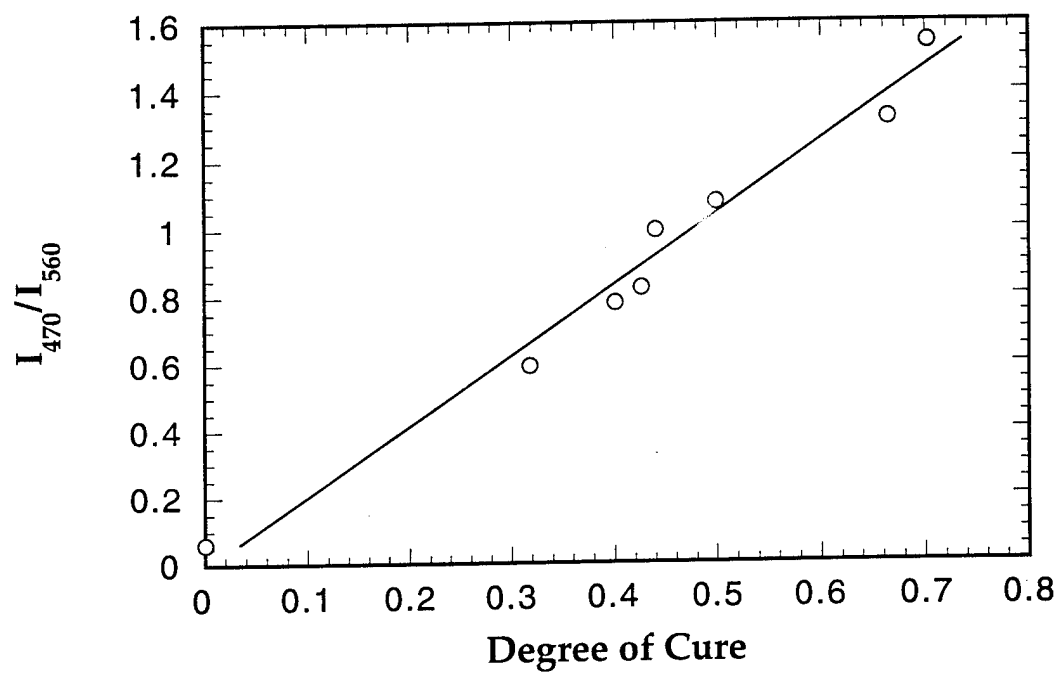(DASB)   (PRODAN)
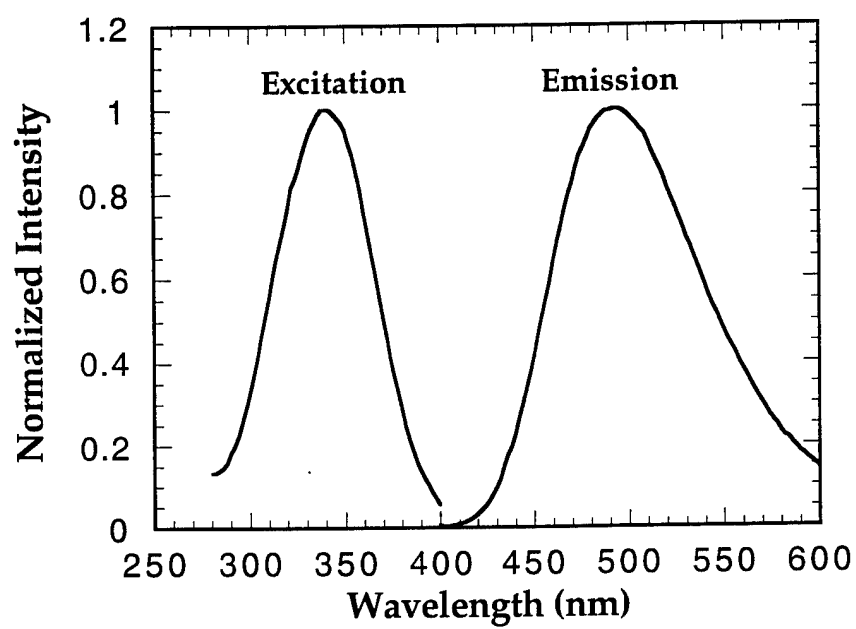
Fig. 1
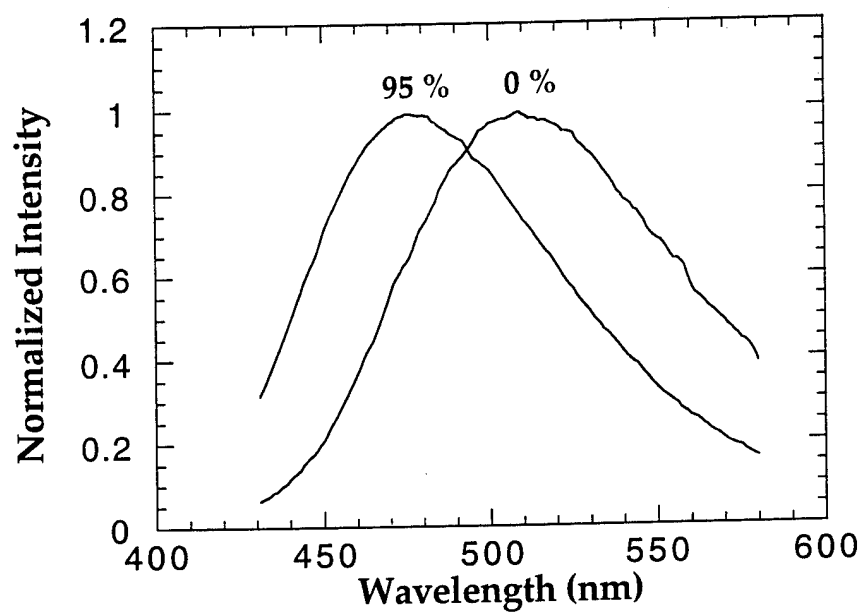
Fig.2
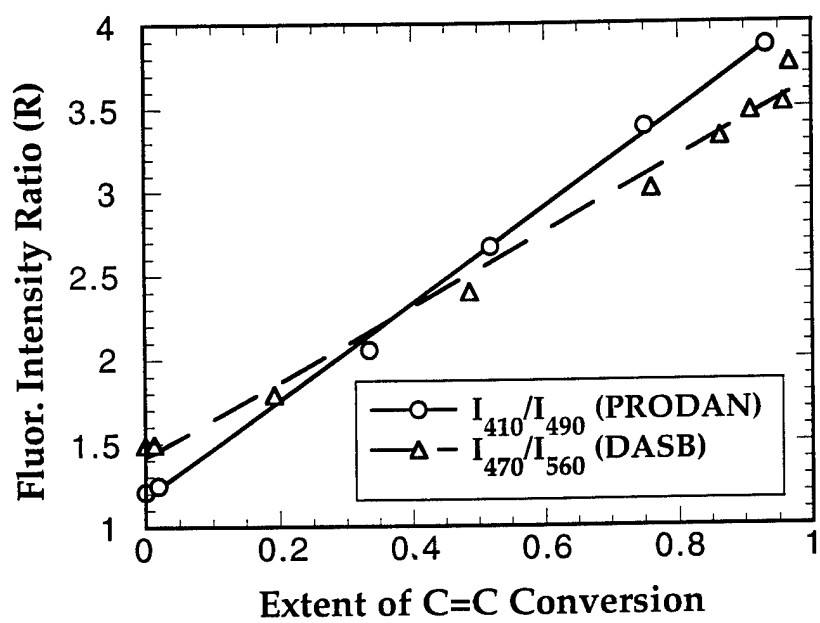
Fig. 3
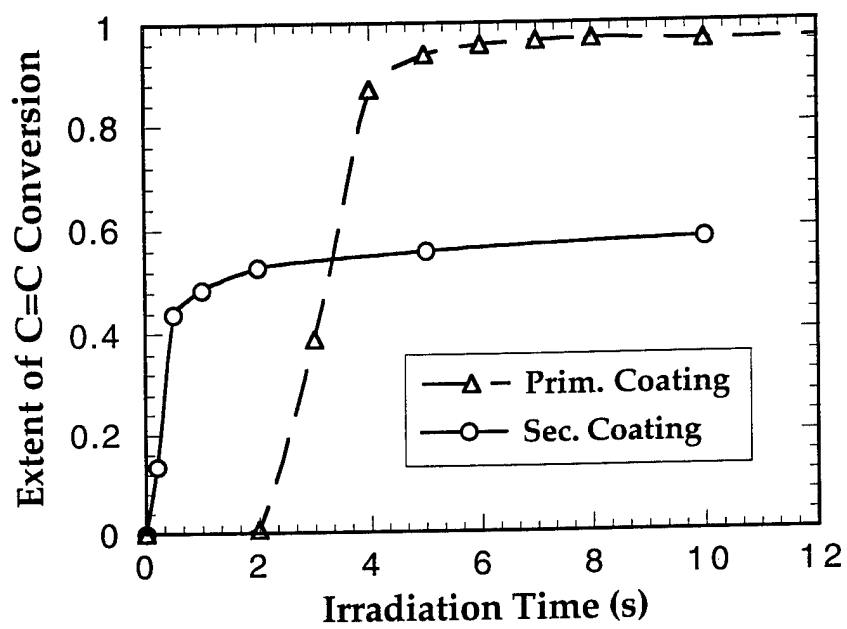
Fig. 4
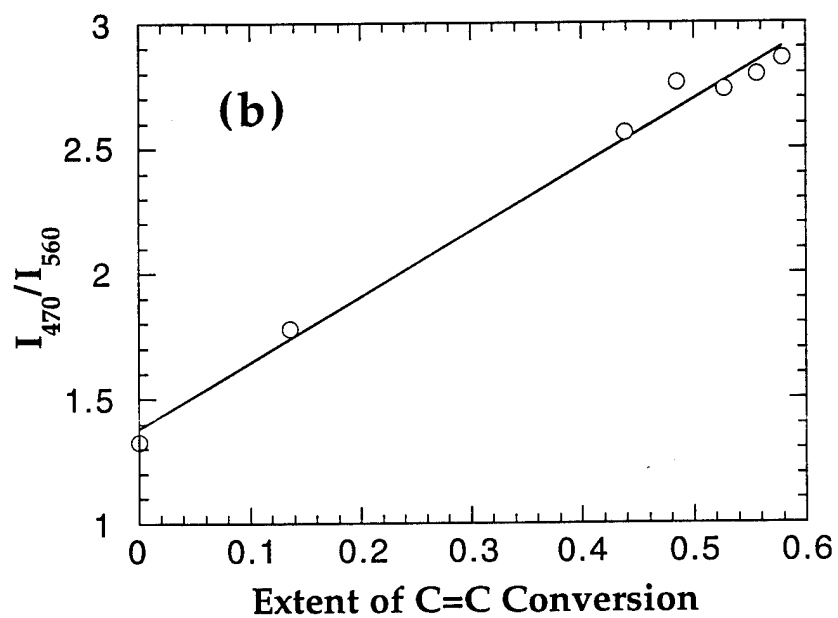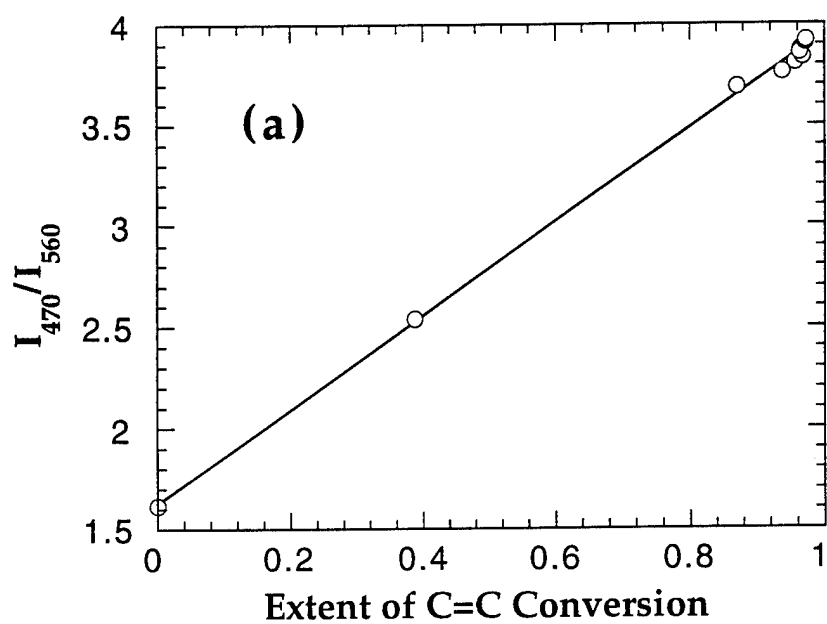
Fig. 5
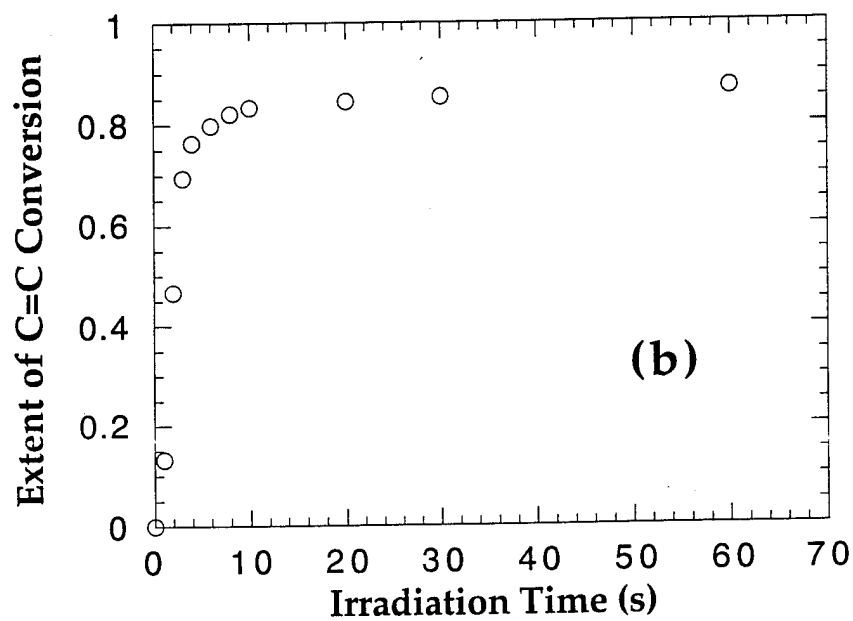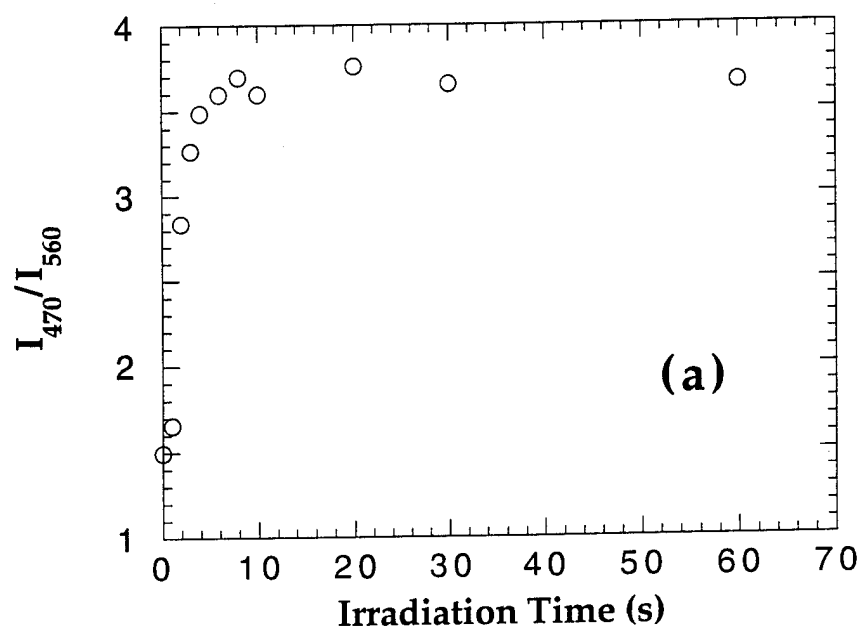
Fig. 6
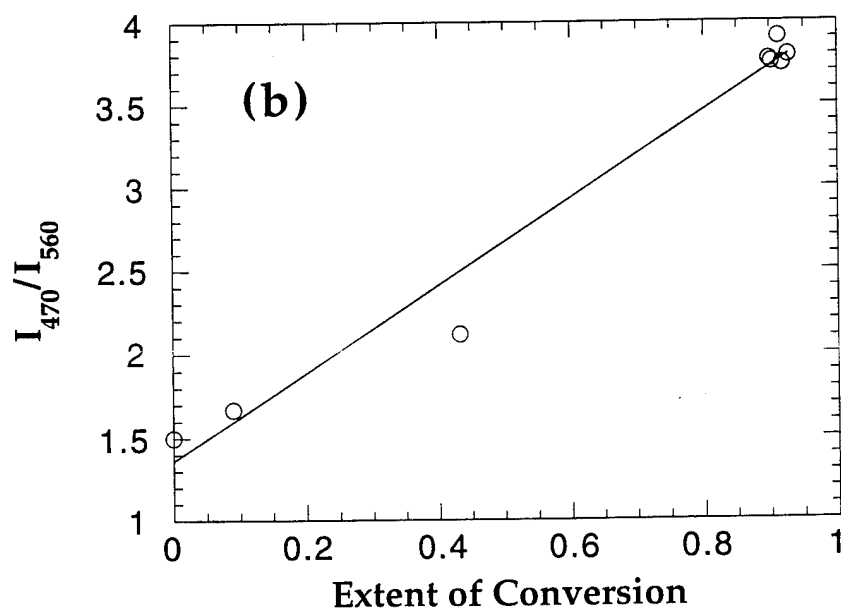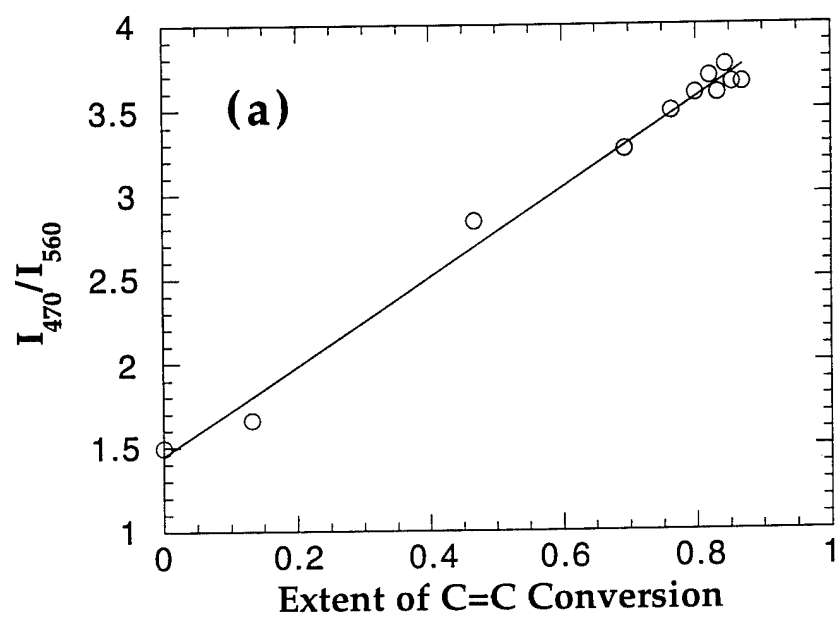
Fig. 7.
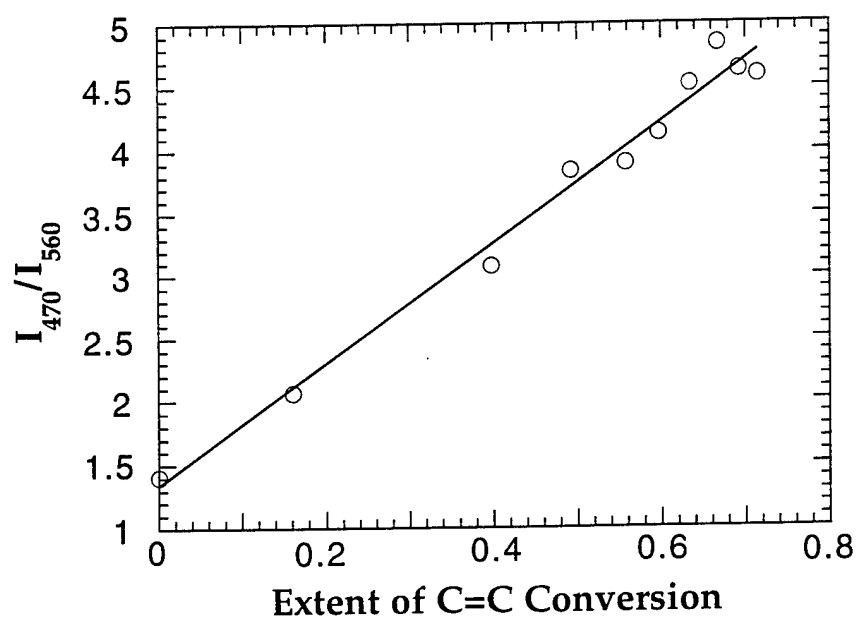
Fig. 8
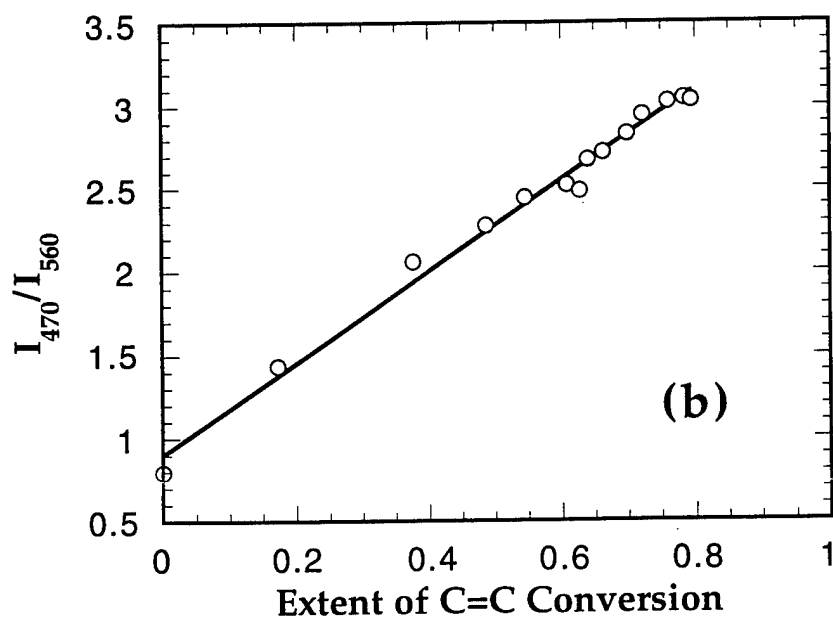
Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13