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Fluorescence Monitoring of Cationic Photopolymerizations: Divinyl Ether Polymerizations Photosensitized by Anthracene Derivatives

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ABSTRACT: Cationic photopolymerizations of vinyl ethers were investigated using *in situ,* time-resolved fluorescence spectroscopy. Due to its short intrinsic time scale, fluorescence spectroscopy provides a means to characterize these polymerizations which are too rapid to be monitored by traditional methods. The fluorescence intensity of the photosensitizer (anthracene or its derivatives) was monitored as a function of time with spectra collected in intervals as short as 2 ms. An observed reduction in fluorescence intensity was attributed to consumption of the photosensitizer, providing a means to monitor the production of active cationic centers. The reaction rate increased as the initiator or photosensitizer concentrations were increased. Also, reactions photosensitized by anthracene and 9,10-dimethylanthracene produced the fastest rates, followed by 9-vinylanthracene. The polymerization rate for 9,10-diphenylanthracene was considerably slower due to steric hindrance or resonance effects. These results illustrate the tremendous potential of *in situ,* time-resolved fluorescence spectroscopy for monitoring polymerizations.

Introduction

Photopolymerizations initiated by ultraviolet (UV) light have received considerable attention for rapid, solvent-free curing of polymer films. These solventless polymerizations proceed rapidly at room temperature with a fraction of the energy requirements of thermally cured systems. The recent surge in applications of UV-initiated photopolymerizations has been motivated by at least two factors: environmental concerns about the production of volatile organic emissions and the need for high-speed reactions to enhance production rates. As a result, UV-initiated photopolymerizations are finding application in a variety of areas, including coatings, inks, adhesives, and electronics (for reviews, see refs 1–4).

To date, most of the work on UV-initiated photopolymerizations has focused on free-radical systems based primarily upon acrylate and methacrylate monomers. These monomers polymerize rapidly and are easily modified at the ester functionality, allowing materials with a variety of properties to be obtained.[1] However, acrylates are not without their problems and shortcomings. Monomeric acrylates are relatively volatile, have an unpleasant odor, and present potential health hazards.[1–3,5] Oligomeric acrylates are much less volatile but exhibit high viscosities. Finally, free-radical photopolymerizations are inhibited by oxygen and often must be carried out under an inert atmosphere such as nitrogen.[1,2,6]

UV-initiated cationic photopolymerizations exhibit several advantages compared to the free-radical photopolymerizations discussed above. First, the cationic photopolymerizations are not inhibited by oxygen;[2,5,6] therefore, it is not necessary to blanket the system with nitrogen to obtain rapid cure rates. Second, in contrast to the free-radical polymerizations which experience a rapid decrease in rate when the light source is removed (due to radical–radical termination reactions), the cationic reactions proceed long after the irradiation has ceased and penetrate recessed areas that the light did not reach. Finally, the cationic technique may be used to polymerize important classes of monomers, including epoxides and vinyl ethers.[5,7–12] These monomers exhibit very low vapor pressures, relatively low viscosities, and negligible toxicity[2] but polymerize very rapidly to form films that exhibit excellent clarity, adhesion, abrasion resistance, and chemical resistance.

Despite the advantages of cationic photopolymerizations discussed above, nearly all the research in UV-initiated polymerizations has focused on free-radical reactions. This fact may be largely attributed to the lack of suitable UV-sensitive cationic photoinitiators until recently.[4,7,8] In the late 1970s, Crivello and Lam reported the development of two novel classes of photoinitiators for cationic polymerizations: diaryliodonium and triarylsulfonium salts (for reviews of the development of these initiators see refs 4 and 13). Upon photolysis, these compounds undergo irreversible photofragmentation to produce aryliodonium or arylsulfonium cation radicals capable of initiating cationic polymerization.[14] However, it was the thermal stability of the initiators that provided the real breakthrough. Although the diaryliodonium and triarylsulfonium salts actively initiate cationic polymerization in the presence of light, they are also remarkably latent in the absence of light, eliminating the necessity of mixing immediately before use.

Diaryliodonium and triarylsulfonium salts are most effective for initiating wavelengths between 225 and 275 nm.[4,9] Therefore, one disadvantage of the onium salt initiators is their poor absorption at wavelengths above 300 nm,[15] where medium- and high-pressure mercury lamps emit much of their radiation. One method of overcoming this limitation is to use photosensitizers to expand the spectral region over which onium salts are effective. Photosensitizers make it possible to initiate polymerization in the near-UV or visible wavelengths of light as a result of a direct interaction between an excited state of a photosensitizer and the initiator. Heterocyclic and fused-ring aromatic compounds often show activity as photosensitizers. Anthracene has been used to photosensitize both free-radical[16] and cationic[17,18] polymerizations. Anthracene absorbs strongly at wavelengths

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between 320 and 390 nm and therefore expands the initiating window to the near-visible region of the spectrum.

To date, most of the work on cationic photopolymerizations reported in the literature focuses on the initiation step of the reaction, and the polymerizations themselves are not well characterized. It is clear that cationic photopolymerizations of vinyl ethers proceed very rapidly; however, few detailed kinetic studies have been performed for these reactions. For example, the kinetics of these photopolymerizations have been characterized in a very cursory manner in terms of the tack-free time of a curing polymer film, but detailed profiles of conversion versus time are not available.

A major reason for the lack of kinetic studies is the extremely rapid reaction rates exhibited by cationic photopolymerizations of divinyl ethers. Because these reactions may proceed to completion in a matter of seconds, there are few experimental techniques with sufficient time resolution to characterize these polymerizations. Differential scanning calorimetry (DSC) has been used extensively to study free-radical photopolymerizations of acrylates[1] as well as cationic photopolymerizations of epoxides;[19,20] however, the technique's relatively slow response time limits its applicability for vinyl ether photopolymerizations. Because the DSC response time is on the order of 2–3 s,[21,22] the technique is only applicable for vinyl ether photopolymerizations that are initiated with relatively low-intensity light[23] when the cure time is relatively long (tens of seconds). Real-time infrared spectroscopy has recently been used to monitor high-speed, laser-induced radical photopolymerizations.[21,24] This technique has a response time of 0.02 s[21] and could therefore be useful for characterizing cationic photopolymerizations. The advantages and limitations of this technique have recently been addressed.[21]

In this contribution, the kinetics of cationic photopolymerizations of vinyl ethers were investigated using *in situ* laser-induced fluorescence spectroscopy. The fluorescence intensity of the photosensitizer was monitored during the reaction to obtain a direct measure of the rate of initiation and to provide indirect information on the rate of propagation. Fluorescence spectroscopy is particularly attractive as an *in situ*, time-resolved technique for monitoring these high-speed polymerizations because it has an extremely short intrinsic time scale (typically 10^{-9} s). The response time for the monitoring technique is invariably determined by the speed of the detection system. In our studies, a high-speed diode array detection system was employed, and fluorescence spectra were collected in intervals as short as 2 ms. Therefore, the fluorescence monitoring method has a considerably faster response time than DSC and real-time IR methods and provides ample time resolution to characterize the cationic photopolymerizations. In addition, since the fluorescence method allows a relatively wide window of wavelengths to be monitored (as opposed to a single wavelength), spectral changes arising from more than one functionality can be monitored simultaneously.

In recent years, several authors[25-28] have reported the use of fluorescence techniques for monitoring polymerizations. Most of these fluorescence techniques monitor polymerization indirectly through the corresponding increase in viscosity. For example, several fluorescence monitoring schemes are based upon fluorescence probes which exhibit enhanced fluorescence intensity with increasing viscosity due to decreased radiationless energy transfer. Wang *et al.*[25,26] have used such a technique to monitor viscosity and chemical changes during polymerization of epoxy and methyl methacrylate systems. Alternatively, Stroeks *et al.*[27] and Wang *et al.*[28] investigated the use of viscosity-sensitive excimer formation to monitor the cure of epoxy resins. However, Stroeks *et al.* concluded that the apparent intensity changes in the excimer peak were actually dominated by changes in the intensity of the overlapping monomer peak (which was enhanced due to reduced radiationless transfer). Finally, Scarlata and Ors[29] have monitored the cure of an epoxy resin by measuring an increase in fluorescence polarization which they attributed to a viscosity-induced decrease in the rotational mobility of the probe molecule. One drawback of the viscosity-sensitive techniques for monitoring cross-linking polymerizations is their limited utility for conversions above the gel point (where there is relatively little change in the local viscosity with time). A novel fluorescence monitoring method not based upon viscosity was recently reported by Sung *et al.*[30,31] Their scheme, which is applicable to amine/epoxy systems, is based upon a reactive chromophore which mimics the reactivity of the amine curing agent. The fluorescence quantum yield of the chromophore increases as the primary amine is converted to a tertiary amine, thereby allowing the reactive state of the amine to be monitored. In more recent work,[32,33] Sung and collaborators have used intrinsic fluorescence and phosphorescence to characterize cure in epoxy composites. Bathochromic shifts in emission spectra were observed as a function of cure time, giving a sensitive method for evaluating the extent of cure.

The fluorescence monitoring scheme reported here is considerably different than the viscosity-sensitive methods reported in the literature. First, because cationic photopolymerizations proceed to completion in a matter of seconds, our studies require considerably faster sampling methods than the aforementioned epoxy resin studies. However, a more fundamental difference between our fluorescence monitoring scheme and the viscosity-sensitive probe approach arises from the fact that we are monitoring the fluorescence of one of the reactants (the photosensitizer), not that of an inert probe. Therefore, this technique provides a more direct measurement of the reaction itself and does not lose sensitivity at the gel point. In the following paper, a description of the fluorescence monitoring technique will be given, along with a discussion of its benefits and limitations.

Experimental Section

Materials. In these studies, 3,6,9,12-tetraoxatetradeca-1,13-diene (DVE-3; GAF Chemicals Corp.) was used as the monomer. The initiator (UV9310C; GE Silicones) had a composition of 5–10 wt % linear alkylate dodecylbenzene, ~50 wt % 2-ethyl-1,3-hexanediol, and ~50 wt % bis(4-dodecylphenyl)iodonium hexafluoroantimonate. Initiator concentrations specified in the remainder of this paper correspond to the total UV9310C concentration. The anthracene, 9-vinylanthracene, 9,10-diphenylanthracene, and 9,10-dimethylanthracene photosensitizers were all purchased from Aldrich Chemical Co. and were used as received.

Absorption and Fluorescence Measurements. Absorption spectra of monomer, initiator, and photosensitizers were obtained using a Hewlett Packard UV–vis 8452A diode-array spectrophotometer. The laser-induced fluorescence studies were performed in the LASER Laboratory at Michigan State University. The fluorescence and photosensitization were both excited with a Coherent Innova 200 argon ion laser operating at 363.8 nm. A Newport 845HP-01 digital shutter system was opened with an electric pulse from the detector controller, ensuring that the initiation and fluorescence acquisition were started simultaneously. Fifteen milliwatts of unfocused laser radiation (measured with a Scientech 362 power/energy meter) in a ~3-mm-

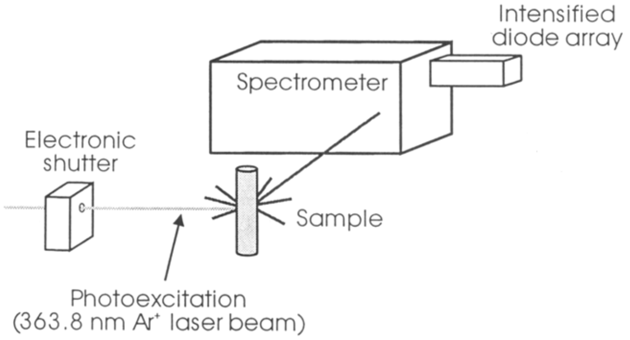

Figure 1. Experimental setup for fluorescence cure monitoring.

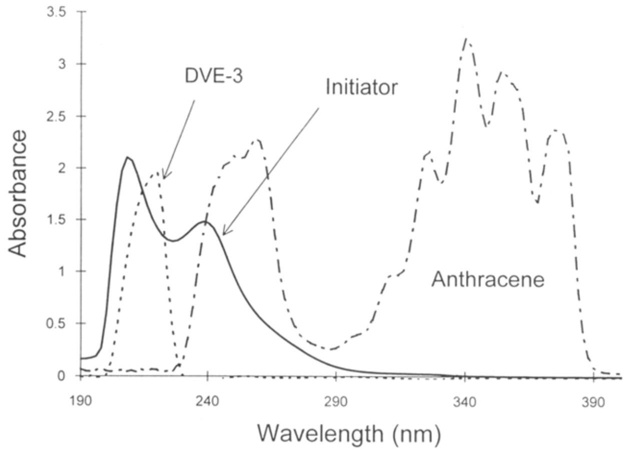

Figure 2. Absorption spectra of monomer (DVE-3), initiator (UV9310C), and photosensitizer (anthracene).

diameter beam was directed to the quartz capillary tube containing the sample, whose longitudinal axis was perpendicular to the laser beam direction. The quartz capillary was approximately 2.5 cm in length with an inner diameter of 1 mm and an outer diameter of 2 mm. A typical reaction system contained ~1 wt % initiator (UV9310C) and ~10^{-2} wt % photosensitizer in monomer (DVE-3). The fluorescent light was collected at an angle of 90° from the incident beam and 90° from the long axis of the quartz tube (see Figure 1). The fluorescence signal was collected using a Spex 1877 Triplemate spectrometer with a subtractive dispersion filter stage and a spectrograph stage. An EG&G Princeton Applied Research Model 1421 intensified diode array, cooled to −20 °C to minimize dark charge levels, was used to detect the signal. The data were analyzed with an EG&G Princeton Applied Research Model OMA III detector controller. To simulate typical process conditions for coating, ink, adhesive, and electronic applications, all reactions were initiated at room temperature and were performed without external heating or cooling.

A fluorescence spectrum spanning 300 nm centered around 450 nm was collected with 150 groove/mm gratings in both the filter and spectrograph stages. The OMA III detection system has the capability of collecting this entire spectrum in 16.67 ms. However, if smaller regions of the spectrum are collected, less time is required per acquisition. Spectral regions from 50 to 100 nm were collected in intervals as short as 2 ms/spectrum.

Results and Discussion

Absorption Experiments. Absorption spectra for the monomer, initiator, and photosensitizer are shown in Figure 2. The figure illustrates that the initiator exhibits a maximum at 210 nm, a second local maximum at 240 nm, and rapidly decreasing absorption up to 290 nm. The monomer (DVE-3) absorption lies completely below 240 nm, leaving a clean spectral region above 300 nm. Anthracene and its derivatives exhibit strong absorption in the 300–400-nm region. Due to this strong absorption, the initiating wavelength for the photopolymerization may be shifted to this region by including anthracene or its derivatives as photosensitizers.

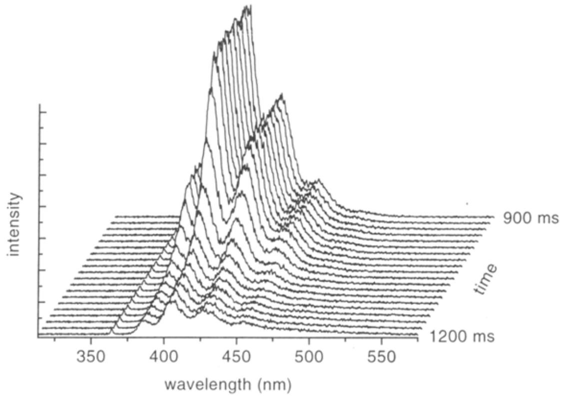

Figure 3. Polymerization of DVE-3 monomer (0.5 wt % initiator) produced by exciting anthracene (2.8×10^{-2} wt %), at 363.8 nm, and monitored by measuring the intensity of the anthracene fluorescence at time intervals of 17 ms.

Fluorescence Experiments. Figure 3 contains a representative series of fluorescence spectra obtained during the cationic photopolymerization of DVE-3. In this figure, each spectrum represents the total fluorescence intensity collected during a 17-ms exposure time; other experiments were performed with intervals as short as 2 ms/scan. This time-dependent plot (with time as the depth axis) consists of 20 spectra for the anthracene fluorescence excited at 363.8 nm (15-mW laser power). As illustrated in Figure 3, under the experimental conditions shown, the anthracene fluorescence was found to decrease slowly for the first 1 s and then drop dramatically over the next 100 ms. Finally, after about 1.5 s, the fluorescence intensity levels off and maintains a relatively low steady-state value. Under other experimental conditions, the time required to attain the final (relatively low) steady-state fluorescence intensity was as short as 0.4 s.

The decrease in anthracene fluorescence intensity illustrated in Figure 3 may be attributed to the consumption of anthracene during the photosensitization reaction. The photosensitization likely proceeds by an electron-transfer mechanism illustrated in Figure 4.[18] The mechanism in Figure 4 illustrates the important photochemical and electron-transfer steps in the reaction. Some possible proton- and hydride-transfer steps which may occur after the radical cation is formed are of no consequence for the monitoring scheme and are omitted from the figure. A more detailed reaction mechanism is reported in ref 34. According to this mechanism, when the anthracene is exposed to 363.8-nm light, it absorbs photons and populates the first excited singlet state. From the first excited singlet state, a fraction of the anthracene undergoes intersystem crossing to populate the lowest triplet state (which may be represented as having unpaired electrons in the 9 and 10 positions). As shown in step 1 of Figure 4, the triplet-state anthracene may then form an excited-state complex with the initiator. In the exciplex, the anthracene may undergo electron transfer to the initiator, forming a radical cation which is capable of initiating cationic polymerization (step 2 of Figure 4). As a result of this set of reactions, the anthracene becomes attached to the polymer as a chain end and loses the aromatic nature of the center ring[18] (steps 4 and 5 of Figure 4). This mechanism (including the role of the triplet state) was recently corroborated by pulsed-laser lifetime studies of the singlet and triplet states.[34]

The above mechanism for photosensitization suggests that the reduction in the fluorescence intensity illustrated

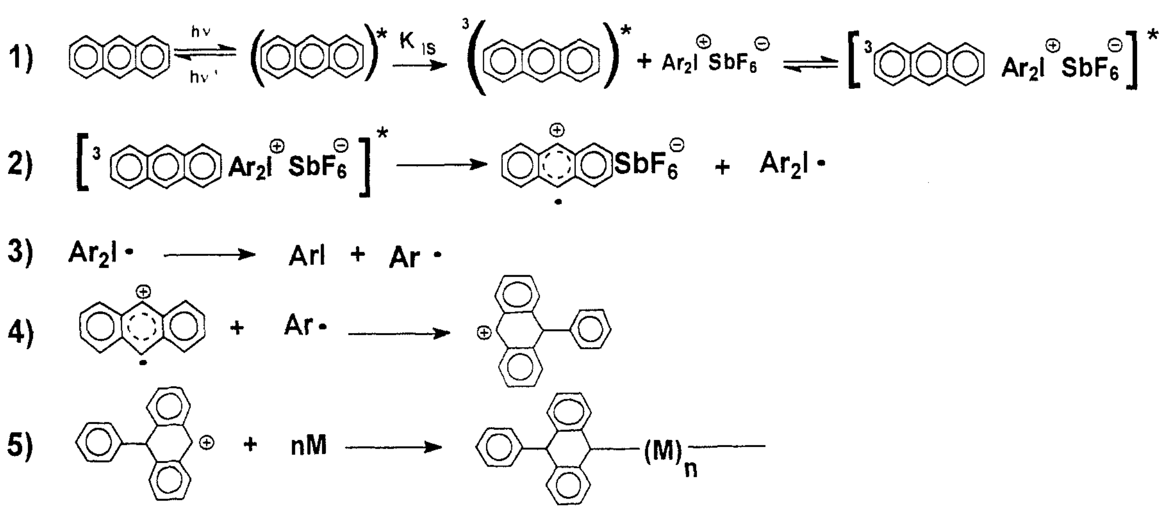

Figure 4. Photosensitization mechanism based on electron transfer from triplet-state anthracene to initiator.

in Figure 3 arises from the loss of the aromaticity of the center anthracene ring during the photosensitization reaction. Therefore, as long as no other anthracene-consuming reactions are taking place, the anthracene fluorescence provides an indication of the number of cationic active centers formed in the reaction system. Each time an anthracene molecule is consumed in the photosensitization reaction, one active cationic center is formed; therefore, the magnitude of the fluorescence decrease at a given time (the difference between the initial steady-state fluorescence and the value at the time of interest) provides a measurement of the number of propagating active centers in the reaction system. In this manner, real-time monitoring of the anthracene fluorescence provides valuable kinetic information. The reduction in fluorescence intensity provides a direct measure of the rate in the initiation step of the reaction as well as an indication of the number of propagating active centers.

A series of experiments were performed to ensure that the fluorescence decrease could be attributed entirely to the photosensitization reaction and that no other anthracene-consuming side reactions were present. Anthracene may participate in a few photoinduced side reactions such as dimerization and oxidation; therefore, studies were performed to determine the extent to which these reactions contributed to the fluorescence decrease. Experiments were performed for two distinct systems: one containing only monomer and photosensitizer and another containing monomer, photosensitizer, and initiator. The system containing no initiator showed very little decrease in fluorescence intensity even after a few minutes of irradiation. In contrast, the system containing all three components exhibited a rapid decrease in fluorescence intensity in a few seconds (much like that shown in Figure 3). These results indicate that, at least for the polymerization time scale, the photodimerization and oxidation reactions do not lead to a decrease in fluorescence intensity and our observed fluorescence decrease may be attributed entirely to the photosensitization reaction.

Initiation and Polymerization Kinetics. Based upon the above discussion, it was concluded that fluorescence spectroscopy could be used for kinetic studies of cationic photopolymerizations by monitoring the fluorescence intensity of the photosensitizer (anthracene or its derivatives). A series of fluorescence spectra such as the ones shown in Figure 3 were analyzed by measuring the fluorescence intensity at a selected wavelength (typically 425 nm) as a function of reaction time. Figures 5–9 contain plots of data collected in this manner. A series of experiments were performed to investigate the effects of a variety of variables on the polymerization kinetics, including the effect of the initiator concentration, the photosensitizer concentration, and the functionalization of anthracene.

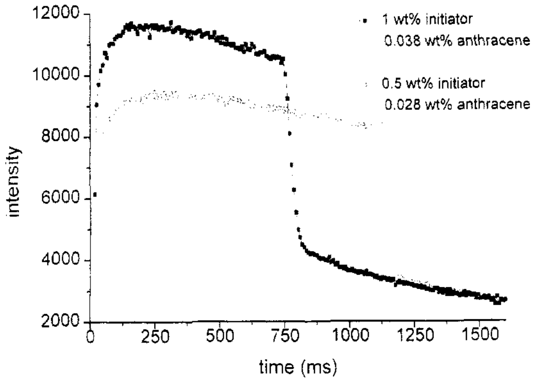

Figure 5. Fluorescence intensity at 425 nm for polymerization of DVE-3 monomer with varying concentrations of initiator (UV9310C) and 10^{-2} wt % anthracene as the photosensitizer.

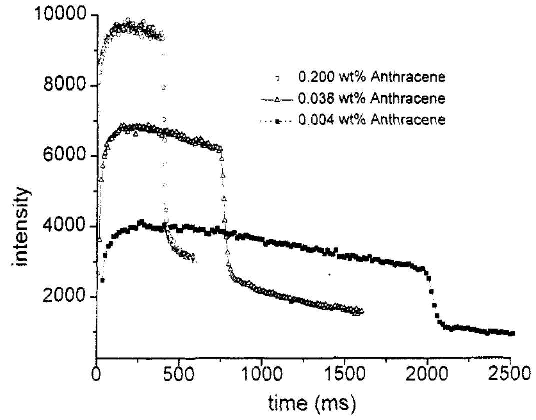

Figure 6. Fluorescence intensity for polymerization of DVE-3 monomer with varying concentrations of anthracene photosensitizer and 1 wt % initiator (UV9310C).

Figure 5 contains plots of the fluorescence intensity versus time for reaction systems containing anthracene ($\sim 10^{-2}$ wt %) and initiator (0.5 or 1 wt %) in DVE-3 monomer. The general shape of the curves in Figure 5 seems to be characteristic of these cationic photopolymerizations. Immediately after the shutter is opened, the fluorescence intensity increases until it attains a relatively constant, quasi-steady-state value. Subsequently, the fluorescence intensity slowly decreases as the anthracene

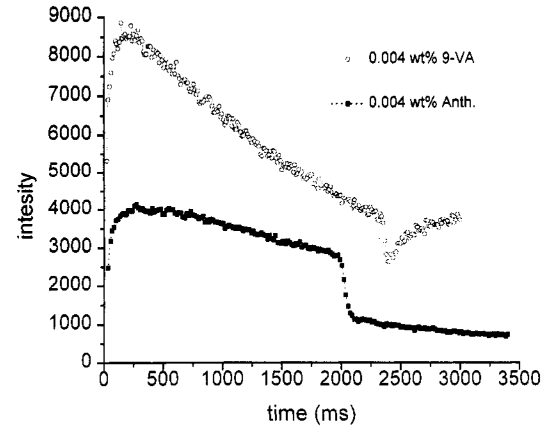

Figure 7. Fluorescence intensity for polymerization of DVE-3 monomer with UV9310C and 10^{-3} wt % 9-vinylanthracene and anthracene as the photosensitizers.

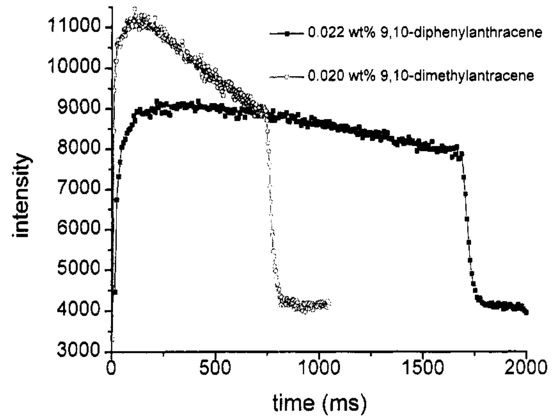

Figure 8. Polymerization of DVE-3 monomer with UV9310C and 10^{-2} wt % 9,10-diphenylanthracene and 9,10-dimethylanthracene as the photosensitizers, monitored by photosensitizer fluorescence intensity.

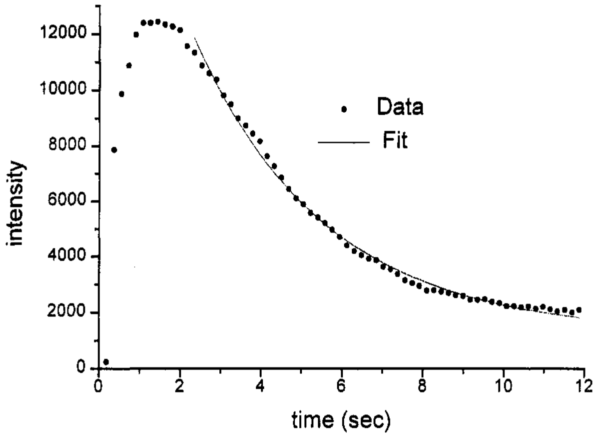

Figure 9. Fluorescence intensity at 425 nm for the photosensitization reaction of 2.2×10^{-2} wt % anthracene as the photosensitizer and 1.2 wt % diaryliodonium hexafluoroantimonate (UV9310C) in methanol.

is consumed and active centers are formed. At some threshold value of time (~750 ms for the 1 wt % initiator case and ~1250 ms for the 0.5 wt % initiator case) the fluorescence intensity falls dramatically (losing ~70% of its value) in less than 100 ms. This seems to indicate that the rate of the photosensitization reaction increases dramatically at this point, possibly due to elevated temperatures arising from the heat of polymerization. A calculation of the adiabatic polymerization temperature illustrates that this temperature increase may be substantial. Based upon estimates of the heat capacity of the monomer ($Cp_m \sim 400$ J/(mol K) by the empirical method of Sternling and Brown[35]) and the heat of polymerization for vinyl ethers ($\Delta H_p \sim 60$ kJ/mol[36]), the adiabatic temperature rise was calculated to be ~150 °C.

If the observed sudden decrease in fluorescence intensity arises from thermal runaway of the initiation and/or propagation reactions, then the rate constants must increase substantially in the adiabatic temperature range. Therefore, a consideration of the activation energies of the photosensitization and propagation reactions is important. The quenching of photoexcited molecules is diffusion controlled with an activation energy of ~15 kJ/mol[37] for small molecules in organic solutions, while the activation energy of propagation for vinyl ethers is approximately 30 kJ/mol.[38] Using an Arrhenius equation for a 125 °C temperature rise (a conservative estimate of the temperature increase), the rate constants of initiation and propagation are found to increase by factors of 6.0 and 35, respectively. The overall rate of polymerization, which depends upon both initiation and propagation, is characterized by an activation energy $E_R = E_I + E_P$, where E_R, E_I, and E_P are the activation energies for the overall polymerization, initiation, and propagation, respectively. Based upon this equation, the activation energy for polymerization is 45 kJ/mol, and the polymerization rate increases by a factor of approximately 210 for a 125 °C temperature change.

In the above discussion of the activation energy for the overall polymerization, termination was assumed to be negligible. In a cationic polymerization active centers do not terminate with one another, and chain transfer normally leads to an active center which is capable of propagation. Therefore, the only possible termination arises from combination with the counterion or reaction with contaminants which give unreactive cations. The possibility of combination with the hexafluoroantimonate ion is low because of the size of the anion, justifying the assumption of zero termination. The inclusion of termination would decrease the value of E_R since the activation energy for termination would be subtracted.

Based upon the above discussion of the reaction energetics, the sudden decrease in the fluorescence intensity exhibited in Figure 5 is attributed to a large increase in temperature which causes a large increase in the reaction rate. To investigate whether the intensity decrease arises in part from temperature-dependent fluorescence, a series of studies were performed in a thermostated cell. In the adiabatic temperature range, the fluorescence intensity of the photosensitizer was found to remain essentially constant or increase slightly. Therefore, the fluorescence decrease exhibited in Figure 5 cannot arise from temperature-dependent fluorescence of the photosensitizer and is attributed to consumption of the anthracene during photosensitization. Therefore, based upon these fluorescence studies, the number of active centers, and therefore the rate of polymerization, may be characterized both by the overall rate of fluorescence decrease and by the time for the onset of the rapid drop in fluorescence intensity. In order to verify the actual temperature rise, *in situ* monitoring of temperature during these cationic photopolymerizations is currently under investigation by laser-induced fluorescence.

Effect of Initiator Concentration. Figure 5 illustrates just how rapidly the reaction occurs when the sample is irradiated with laser light. A cursory observation would suggest that, in both cases, the liquid monomer sample becomes a solid polymer almost immediately after the shutter is opened. The detailed time resolution provided by the laser experiment illustrates that, as expected by simple kinetic considerations, the polymerization rate is noticeably higher for the sample containing the higher concentration of initiator (as indicated by the time for the rapid decrease in fluorescence). In either case, the reaction is very rapid, with most of the fluorescence decrease occurring in less than 1.25 s.

Effect of Photosensitizer Concentration. Figure 6 contains plots of fluorescence intensity versus time for systems containing 1 wt % initiator and various concentrations of anthracene in monomer. The figure illustrates that, as the anthracene concentration is increased from 0.004 to 0.038 wt %, the time for the onset of the rapid fluorescence decrease changes nearly 3-fold from ~2000 to ~750 ms. Therefore, the reaction rate is very sensitive to the anthracene concentration and increases significantly as the anthracene concentration is increased an order of magnitude from 0.004 to 0.038 wt %. If the photosensitizer concentration is increased another order of magnitude (to ~0.2 wt %), the time required for the rapid drop in fluorescence decreases further (~400 ms), but at a smaller incremental rate (by less than a factor of 2). Therefore, the reaction rate becomes less sensitive to the photosensitizer as the anthracene concentration is increased. This trend may be explained by the fact that the high anthracene concentrations lead to a high optical density (OD ~2 for 100-μm sample thickness in the 0.2 wt % anthracene case) which limits the penetration of the light into the sample. Therefore, many of the anthracene molecules near the back of the sample are not excited and cannot produce active cationic centers. This hypothesis is supported by the fact that the polymerization was limited to approximately the front half of the sample.

Effect of Anthracene Functionalization. Experiments were performed using a variety of anthracene derivatives as photosensitizers. The purpose of these experiments was to determine the effect of anthracene functionalization on the rate of the cationic photopolymerizations. In Figure 7, the fluorescence intensity for reaction systems containing 0.004 wt % anthracene or 9-vinylanthracene as the photosensitizer is plotted versus time. The figure illustrates that the reaction is somewhat more rapid for anthracene than for 9-vinylanthracene since the rapid decrease in fluorescence occurs in about 2 s for anthracene and in about 2.3 s for 9-vinylanthracene. It is interesting to note that the curve for 9-vinylanthracene exhibits a steeper slope and a larger fluorescence decrease in the early stages of polymerization. This may arise from its ability to participate in the propagation of the active center through its vinyl functionality.

Fluorescence studies were also performed using two other anthracene derivatives as photosensitizers: 9,10-diphenylanthracene and 9,10-dimethylanthracene. The fluorescence intensity of 9,10-diphenylanthracene has been shown to be relatively insensitive to changes in viscosity;[25] therefore, these studies were performed in part to investigate the possibility that the decreases in fluorescence intensity observed in Figures 5 and 7 are due to viscosity effects. In Figure 8, the fluorescence intensities for systems containing 10^{-2} wt % 9,10-diphenylanthracene or 9,10-dimethylanthracene as photosensitizers are plotted versus time. The figure illustrates that, as in the previous experiments with anthracene, the fluorescence intensity of these probes initially exhibits a gradual decrease with time and then shows a dramatic drop as the reaction proceeds. The fact that the general shapes of the fluorescence profiles are the same as those for anthracene and 9-vinylanthracene indicates that viscosity effects are not responsible for the decrease in fluorescence.

Comparison of Figures 5 and 8 illustrates that, for the 9,10-diphenylanthracene system, the decay time was 2.5 times longer than that of the 10^{-2} wt % anthracene system and nearly 2 times longer than that of the 9-vinylanthracene system. In contrast, the 9,10-dimethylanthracene decay time was the same as the decay time for anthracene. These results indicate that the 9,10-diphenylanthracene photosensitizer reaction is hindered due to steric effects of the phenyl rings or formation of a stable radical cation due to electronic stabilization. The methyl groups of 9,10-dimethylanthracene seem to have little effect on the reaction, when used as the photosensitizer. These results are consistent with the electron-transfer mechanism for photosensitization shown in Figure 4.

Fluorescence Experiments without Monomer. The photosensitizer fluorescence intensity was also monitored for a system containing photosensitizer and initiator but no monomer. The reaction system without the divinyl ether monomer will not include any temperature effects arising from the heat of polymerization. Since these polymerizations are highly exothermic and very rapid, the reaction may take place under nearly adiabatic conditions with a significant increase in temperature. This increase in temperature could in turn increase the reaction rate further. Figure 9 contains a plot of anthracene fluorescence intensity versus time for 0.02 wt % photosensitizer and 1.2 wt % of initiator in methanol. Comparison of Figure 9 with Figures 5–8 reveals a dramatically different fluorescence profile for the system without monomer. The system containing only photosensitizer and initiator exhibits a fluorescence intensity which decays exponentially over a time period of 12 s, with no sharp decrease at an intermediate time as was observed for the systems which also contained DVE-3. This suggests that the rapid decrease in fluorescence seen in Figures 5–8 is due to a temperature increase arising from the heat of polymerization. This hypothesis is supported by the fact that the time scale of the photosensitization reaction in methanol is seconds as compared to milliseconds for the divinyl ether reaction systems. The time constant for the best fit experimental decay was found to be 4.7 s for the curve in Figure 9.

Conclusions

We have demonstrated the utility of *in situ* laser-induced fluorescence spectroscopy for monitoring cationic photopolymerizations of vinyl ethers photosensitized by anthracene and its derivatives. Due to its extremely short intrinsic time scale, fluorescence spectroscopy provides a means to characterize the kinetics of these polymerizations which are too rapid to be monitored by traditional methods such as DSC. In our studies, the fluorescence intensity of the photosensitizer was monitored as a function of time with spectra collected in intervals as short as 2 ms. The profile of the fluorescence intensity versus reaction time invariably exhibited the same general shape with an initial increase to a quasi-steady-state value, followed by a gradual decrease over several hundred milliseconds, followed in turn by a dramatic reduction in a period of less than 100 ms to a final, relatively constant value.

The observed reduction in fluorescence intensity is attributed to the consumption of the anthracene in the photosensitization process, with the associated production of active cationic centers. Experiments were performed to demonstrate that anthracene-consuming side reactions such as photoinduced dimerization did not contribute to the reduction in fluorescence. Therefore, it was concluded that the magnitude of the fluorescence decrease provides a direct measure of the rate of the initiation step, as well as an indication of the number of propagating active centers. The sharp decrease in fluorescence was attributed to large temperature increases arising from the heat of polymerization in these nearly adiabatic reactions (experiments were performed without external heating or cooling to simulate typical process conditions in coating, adhesive, and electronic applications). This conclusion was corroborated by experiments performed with initiator and photosensitizer but in the absence of monomer. In these experiments, which would have no effects from the heat of polymerization, the fluorescence intensity exhibited no sharp reduction in intensity but rather decreased exponentially over a period of 12 s.

The rates of the cationic photopolymerizations were characterized in terms of the overall rate of the fluorescence decrease and the time for the onset of the rapid reduction in fluorescence intensity. Experiments were performed to determine the effects of the initiator concentration, the photosensitizer concentration, and anthracene functionalization on the polymerization rate. As expected, the reaction rate was found to increase as the initiator concentration or the photosensitizer concentration were increased. A practical concentration limit for the photosensitizer of approximately 0.2 wt % for 500-μm films was established due to high optical densities which limit the penetration of light into the sample. Reactions photosensitized by anthracene and 9,10-dimethylanthracene produced the fastest rates, while the slowest rates were observed for 9,10-diphenylanthracene, perhaps due to steric hindrance or electronic interference caused by the phenyl rings. The 9,10-diphenylanthracene studies also illustrated that the fluorescence intensity decrease was insensitive to viscosity changes.

The fluorescence monitoring technique described here offers a nonintrusive, time-resolved method for monitoring cationic photopolymerizations. Based upon this technique, our studies have provided previously inaccessible information about the rate of the cationic photopolymerizations and the effects of various reaction conditions. However, the technique has limitations. For example, although these studies based upon the magnitude of the photosensitizer fluorescence provide direct information about the rate of generation of active centers, they provide little information about the rate at which the active centers propagate once they are formed. Also, although the response time is considerably faster than the current alternatives, it is limited by the speed of the detection system (2 ms in our case). Finally, although the studies reported here illustrate the tremendous potential of *in situ*, laser-induced fluorescence spectroscopy for monitoring polymerizations, they provide only one example of a much more general technique. Many other fluorescence monitoring schemes which provide complementary information could be developed. For example, the use of laser-induced fluorescence for the *in situ* monitoring of temperature during these cationic photopolymerizations is currently under investigation in our laboratory, and strategies for using reactive probes to monitor the propagation reaction are under development. Clearly, there is considerable potential for novel applications of time-resolved fluorescence spectroscopy for monitoring polymerizations. We hope that this contribution prompts others to consider this relatively unexplored technique for their applications.

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