

Photopolymerization kinetics and monomer diffusion in polymer matrix

V. V. Krongauz* and R. M. Yohannan

*E. I. DuPont de Nemours and Company Inc., Imaging Systems Department,
Experimental Station Laboratory, Box 80352, Wilmington, DE 19880-0352, USA
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A direct and non-destructive method for observing reaction kinetics and monomer transport in photopolymers during photopolymerization is presented. This method is based on monitoring a change in intensity of the fluorescence emitted by plasticized vinylacetate film containing fluorescent monomer, *N*-vinylcarbazole. The film used in the experiments had high optical density at 295 nm. Illumination of one side of the film led to polymerization of the dispersed monomer and reduction of its concentration predominantly near the illuminated surface. Thus, during this photopolymerization reaction, which produces a monomer concentration gradient, the monomer diffuses across the film toward the illuminated surface. Since only the monomer and resulting polymer are fluorescent, an increase in concentration of the polymer near the illuminated surface increases the fluorescence intensity. This increase in fluorescence intensity is used to monitor the photopolymerization kinetics. It is demonstrated here that upon excitation at 295 nm at room temperature the polymerization kinetics of *N*-vinylcarbazole in a plasticized vinyl acetate film are controlled by *N*-vinylcarbazole diffusion. The diffusion coefficient for this monomer, as measured in the present work, is $6 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

(Keywords: photopolymers; film; photopolymerization; fluorescence; kinetics; diffusion; *N*-vinylcarbazole; poly(*N*-vinylcarbazole))

INTRODUCTION

Polymer photoimaging materials and systems are widely used in printing and electronic industries¹. We have investigated photopolymerization kinetics in an industrially important photopolymerizable system called a 'photopolymer'. Photopolymers are generally composed of a high molecular weight polymer matrix (binder) containing a plasticizer, photo-initiator, monomer and a range of chain transfer and termination agents. Cohen and Walker¹ applied the term 'photopolymer' exclusively to the systems based on photopolymerization of vinyl monomers.

The photopolymer system studied by us contained *N*-vinylcarbazole (NVC) monomer, which is polymerized to yield poly(*N*-vinylcarbazole) (PVCA). Cellulose acetate butyrate (CAB) or polyvinylacetate (VINAC) were used as the inert matrix. Both NVC and PVCA strongly fluoresce around 350–500 nm.

In photopolymerization conducted in a plasticized polymer matrix, the processes of chain initiation, propagation and regeneration can be controlled by the slow diffusion of monomer molecules^{2,3}. Thus knowledge of the diffusion rate of a monomer in a given polymer matrix becomes crucial for understanding the photopolymerization mechanism and design of a polymeric system for photo-imaging applications. A variety of methods have been applied to investigate monomer diffusion and polymerization kinetics in such systems^{3–6}. Below, we describe the direct and non-destructive observation of reaction kinetics and monomer transport in a photopolymer during photopolymerization through monitoring fluorescence emitted by a photopolymer film.

EXPERIMENTAL

Materials and reagents

The photopolymeric system contains an ultraviolet (u.v.) sensitive non-fluorescent initiator, a chain transfer agent and plasticizers^{1,7,8}. NVC is the only fluorescent polymerizable component. It is obtained from Monomer-Polymer and Dajak Laboratories Inc. Poly(*N*-vinylcarbazole), used as the standard in the studies, is obtained from Aldrich Chemical Company Inc. The films are made using cellulose acetate butyrate (CAB) or polyvinylacetate (VINAC) as the inert polymer matrix.

Optosil-2 (Amersil Inc.) quartz slides are used as film support. The polymer solutions are spin coated on these slides to yield films with thicknesses $< 25 \mu\text{m}$ or coated using a doctor knife coater for preparation of the thicker films. The film thickness is measured using a Sloan Dektak 3030. The films are cast from 7% (by weight) solution in methylene chloride and dried at ambient conditions for 5–6 h. Methylene chloride (EM Science, glass distilled, spectroscopically pure) is additionally purified using a 60 cm long silica column.

Apparatus and run procedures

The absorption spectra are measured using an IBM u.v./visible 9420/9430 spectrophotometer. The optical density at 295 nm of the 20 μm thick (the thickness most often used in our experiments) photopolymeric film is very high, ≥ 14 . The absorption of even 0.7 μm thick films is 0.5 at 295 nm (Figure 1).

In all our experiments the photopolymeric film is illuminated by u.v. light (295 nm) on one side of the film, while the transmitted fluorescence, emitted by the sample, is monitored from the opposite side of the film. Internal

* To whom correspondence should be addressed

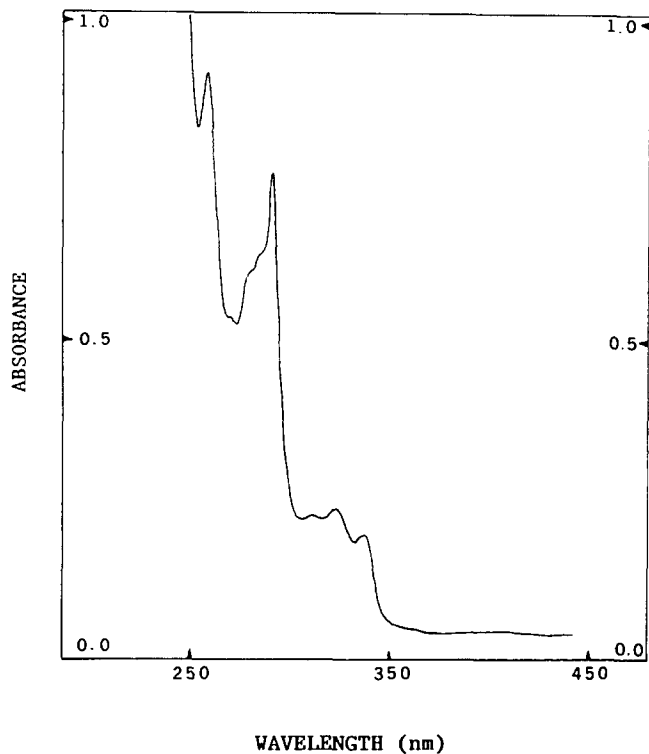


Figure 1 Absorption spectrum of 0.7 μm photopolymer film

absorption of the fluorescence by the sample at the monitoring wavelength (400 nm) is negligible even for 60 μm thick films. Emission spectra are measured using a Perkin-Elmer fluorescence spectrophotometer, model 650-40. The emission of NVC has a well defined peak around 350 nm. The emission of PVCA in the polymeric matrix has a broad peak around 350–450 nm, largely from the excimer^{3,4}. The fluorescence spectra in solution and in polymer matrix are presented in Figures 2a and b. Time-dependent emission spectra are measured during the polymerization reaction using a Princeton Instruments IRY-512 diode-array detector (Figure 2c).

A schematic diagram of our experimental set-up for monitoring of photopolymerization kinetics is presented in Figure 3. A 150 W Xe-arc lamp (Oriental Co.) is used as a light source. The light passes through a 5 cm long water filter, a 295 nm bandpass (bandwidth ≈ 100 nm) interference filter and a monochromator (diffraction grating, Bausch and Lomb). The light continues through 0.1 ms shutter (Vincent & Assoc.) and is focused by two quartz lenses onto a quartz slide coated with the photopolymer film (coating is on the side of the slide directed away from the Xe lamp). In some experiments the photopolymer film is sandwiched between two slides. Fluorescence detection is conducted in the transmission mode. The slide is positioned at roughly 45° to the direction of propagation of the excitation light. The sample fluorescence is detected at the same angle to reduce the collection of scattered excitation light. The fluorescence light passes through a glass bandpass filter with bandwidth 360–550 nm, and then through a monochromator (Bausch and Lomb Co.). The detection is conducted at 400 ± 5 nm. A Hamamatsu R329-1 (2" head-on) photomultiplier tube, operating at 1650 V, is used for detection. The photomultiplier tube is placed into a housing with a manual shutter (Products for Research). A 0.1 A, 2500 V power supply (Bertan

Associates, Model 215) is used. The signal is amplified using a Stanford Research preamplifier SR440. The signal is monitored using 200 MHz oscilloscope (Hitachi, V-1065). Signal processing is done using a Stanford Research Systems photoncounter (SR400) interfaced with a Hewlett-Packard Vectra RS-16 microcomputer. The data are transferred to a VAX-11/780 computer for the mathematical treatment.

A typical experimental run starts with the collection of the background signal (usually ≈ 50 counts s^{-1}). The excitation light shutter is opened and fluorescence is monitored as a function of time.

Special care is taken to ensure that *N*-vinylcarbazole and polyvinylcarbazole are not destroyed by the high intensity u.v. light. That is why a high optical density bandpass filter is used to attenuate the light. A series of experiments is performed to ensure that carbazole and poly(*N*-vinylcarbazole) are not decomposed during the experiment.

RESULTS AND DISCUSSION

Principle of technique

U.v. irradiation of a photopolymer film leads to an increase in intensity of fluorescence emitted by a sample (Figure 2c). We attribute this increase to monomer migration toward the illuminated surface of the photopolymer during polymerization. Due to the high optical density, the excitation u.v. light is completely absorbed near the surface of the polymeric film. As a result, during photopolymerization, the monomer is consumed more rapidly near the exposed surface of the film. This creates a monomer concentration gradient, and the monomer migrates toward the illuminated surface of the film. The contribution of the monomer and resulting polymer to the optical density of the film at 295 nm is $< 10\%$. As PVCA forms and more NVC migrates to the illuminated surface, the amount of light absorbed by fluorescent carbazyl groups increases and thereby the fluorescence emission increases as well (Figure 2c).

The photopolymer usually contains small amounts of fluorescence quenchers dispersed throughout the film. There is no mechanism for quencher migration during the exposure. As carbazyl groups (in NVC) migrate, due to photopolymerization, the local concentration of carbazyl groups near the illuminated surface becomes higher than that of a quencher. This fluorophore-quencher separation should also contribute to the increase in fluorescence intensity. The second factor is also proportional to the change in concentration of the carbazyl groups near the surface. Both factors, better illumination at the surface and decreased relative concentration of quencher per carbazyl group, can be treated as a total effect indicating the extent of the diffusion from the bulk of the film.

Under conditions of diffusion controlled kinetics, and with the photopolymeric film thickness known, the monomer diffusion coefficient is deduced^{9,10}.

Results and physical model

The observed increase in fluorescence intensity cannot be ascribed to the polymerization of NVC, or to any other process, without invoking diffusion of additional NVC to the illuminated surface. The emission spectra of the photopolymers exhibits some shift during the photo-

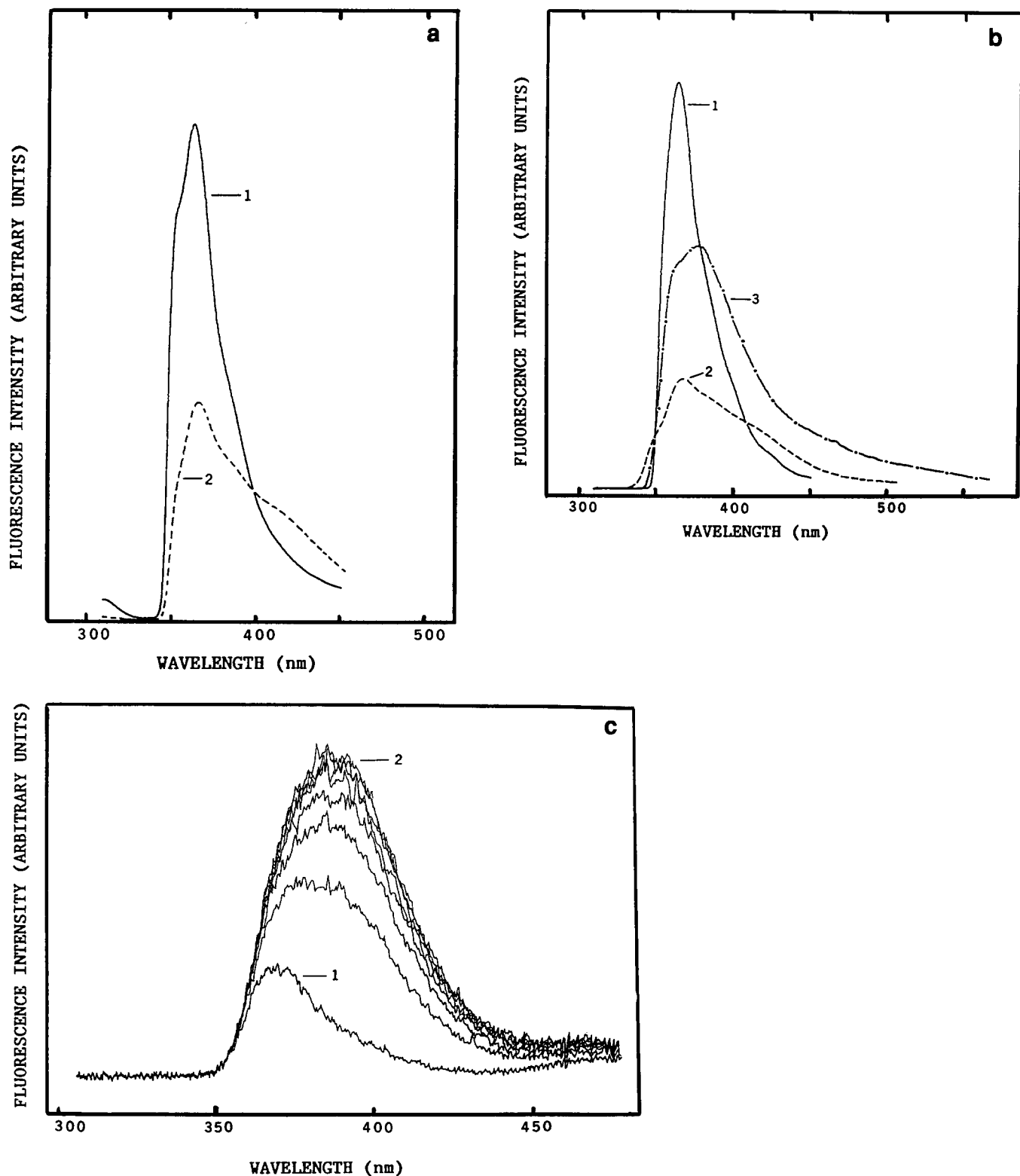


Figure 2 (a) Emission spectra of equimolar solutions of NVC (1) and PVCA (2) in methylene chloride; (b) Emission spectra of equimolar solutions of NVC (1) and PVCA (2) in VINAC film. 3, Spectrum of exposed photopolymer, magn. approx. $\times 5$; (c) Time dependence of the emission spectrum of photopolymer film: 1, beginning of exposure to 295 nm u.v. light; 2, end of reaction. The initial and final spectra were taken 600s apart. In between the spectra were taken every 30s. Each spectrum was recorded during a 1 s time interval

polymerization (Figure 2c). However, the observed increase in emission intensity cannot be explained by the spectral shift due to poly(*N*-vinylcarbazole) formation from *N*-vinylcarbazole. Both materials have almost identical extinction coefficients at 295 nm ($\approx 6.1 \times 10^4$ for PVCA versus $\approx 6.9 \times 10^4$ for NVC), and the fluorescence intensity of solution of PVCA at 400 nm is slightly lower than that of NVC solution with equal concentration

(percentage by weight). The emission of PVCA in a polymeric matrix is due to the excimer emission³ and has a lower quantum yield than in solution. In our experiments, it is observed that as the viscosity of the solution goes up (addition of VINAC or CAB) the emission of NVC broadens as well. This phenomenon can also be explained by excimer formation. In any event, since NVC fluorescence yield at 400 nm is higher

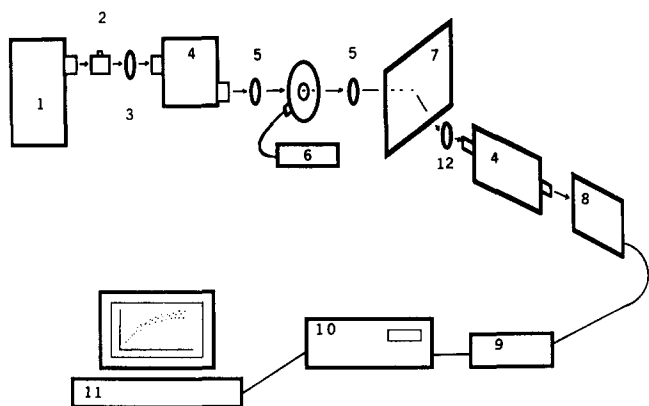


Figure 3 Schematic diagram of the experimental set-up: 1, 150 W Xe arc light source; 2, water filter; 3, 295 nm band-pass interference filter; 4, Bausch and Lomb monochromator; 5, silica lens; 6, electro-mechanical shutter; 7, silica slide coated with photopolymer film; 8, photomultiplier tube, housing and shutter; 9, preamplifier; 10, photon counter; 11, microcomputer; 12, 360 nm high-pass glass filter

than that of PVCA, in either solution or in a rigid matrix, polymerization of NVC to yield PVCA could not account for the signal increase.

The observed increase in fluorescence intensity can be attributed only to the migration of additional NVC towards the illuminated surface where it polymerizes to PVCA upon illumination. The emission spectra of the films containing various relative concentrations of PVCA and NVC (the sum of PVCA and NVC concentrations is kept constant) are measured to ascertain that the increase in emission is connected with the monomer migration to the illuminated region rather than a spectral shift from NVC to PVCA. Some additional experiments described below support this conclusion.

A small rectangle of film (0.7, 24 and 39 μm thick) squeezed between two quartz slides is illuminated until the emission increase stops, then flipped and exposed from the opposite side of the film. The fluorescence emission increases upon the exposure of the 'front' surface. The exposure of the opposite (flip) side of the same area of the film results in a slightly lower initial fluorescence emission, a slower increase in emission and a lower ratio of final to initial fluorescence (*Figure 4*). This result indicates that diffusion to the exposed side of the film indeed occurs in this system, thereby depleting the overall amount of the monomer in the film. Therefore, diffusion towards the flip side of the film after it is exposed to light, starts with a lower initial monomer concentration (lower initial value of the signal on *Figure 4*, curve 2) and proceeds to a lower final signal than the first process.

Exposure of the thinner film with an optical density of 0.5 from one side resulted in polymerization through the entire film thickness (*Figure 5*). The emission intensity growth upon the first exposure of the film indicates that some monomer was migrating towards the front surface (*Figure 5*, curve 1). Exposure of the flip side of the film did not result in a fluorescence intensity increase (*Figure 5*, curve 2). Apparently, relatively little free monomer remains in the bulk of the film after the front surface exposure, so no polymerization takes place and no increase of the fluorescence intensity occurs. The intensity of the emission is lower than the limit value obtained after the front surface exposure (*Figure 5*, curve 2) (the

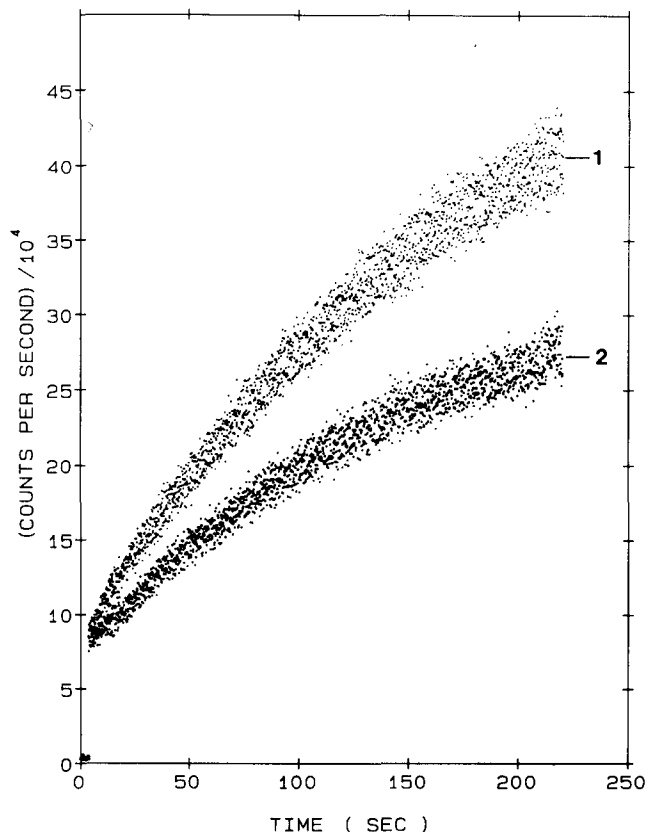


Figure 4 Time dependence of fluorescence intensity during photopolymerization in 39 μm film: 1, front surface exposure; 2, flip surface exposure

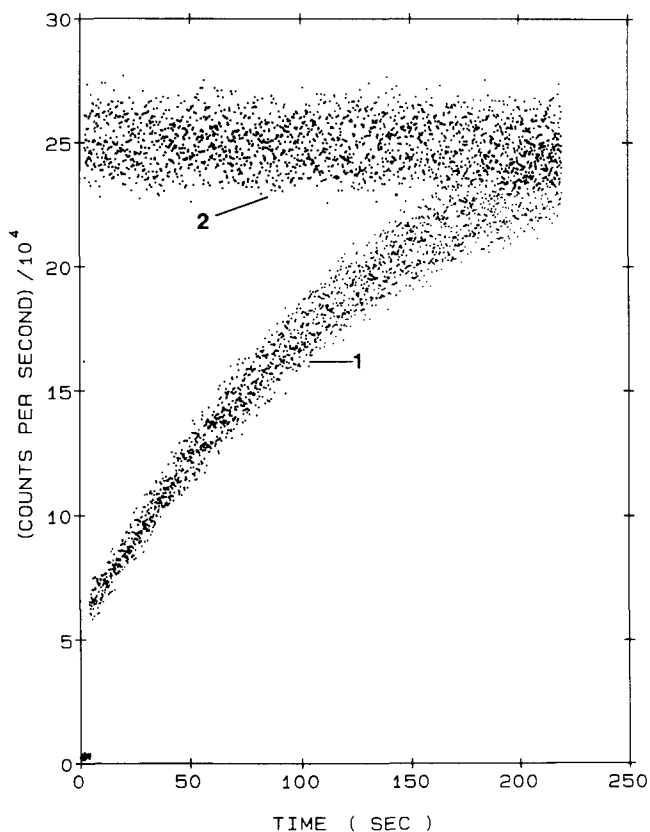


Figure 5 Time dependence of fluorescence intensity during photopolymerization in 0.7 μm film: 1, front surface exposure; 2, flip surface exposure

limit of the front surface exposure polymerization is not shown).

The data for the thin film deserves some additional comment. In the thick films, migration of monomer toward the initially exposed surface depletes monomer concentration in the bulk of the film. This is reflected in the lower initial fluorescence intensity of the flip surface (Figure 4, curve 2). We do not observe a similarly lower emission intensity of the flip side for a thin film. There is a substantial difference between 'thin' ($0.7\ \mu\text{m}$) and 'thick' ($>20\ \mu\text{m}$) films. In a thick film the initially exposed surface does not contribute to the fluorescence of the flip side, since the optical density at 295 nm is high, and only molecules on the illuminated side are excited. In a thin film with lower optical density (≈ 0.5), the excitation light penetrates through the thickness of the film and all carbazyl groups in the thin film may contribute to some extent to the fluorescence. During the front surface exposure the polymerization concentrates the carbazyl groups relative to the local concentration of the quencher, thereby increasing the emission intensity as was discussed above (Figure 5, curve 1). When the flip side of the thin film with low optical density is exposed, these highly fluorescent, quencher-free carbazyl groups in PVCA are also excited and result in higher emission intensity than one would observe if only non-polymerized NVC were involved (like during the front surface exposure). This may be a reason why the emission intensity of the flip side of a thin photopolymer film is higher than the initial emission intensity of the front surface (Figure 5), unlike the case of the thick film (Figure 4). The limit intensity value of the front surface exposure is characterized by $3.2 \times 10^5 \pm 200\ \text{counts s}^{-1}$ versus $2.4 \times 10^5 \pm 200\ \text{counts s}^{-1}$ for flip side exposure, since some monomer did migrate

away from the flip surface during the exposure of the front surface and the excitation light was attenuated by the film. A more detailed investigation of this mechanism is being conducted.

It is interesting that plots of the data normalized to 1, using $[I(t) - I(0)]/[I(\infty) - I(0)]$, where $I(t)$, $I(0)$, $I(\infty)$ represent fluorescence intensity at time t , 0, and ∞ , coincide for both exposures of the same film (films $\geq 20\ \mu\text{m}$). This is readily explained since both sets of data have to result in the same diffusion coefficient. The data have to yield the same fraction of process completion independent of initial concentration of monomer.

When the photopolymer, dissolved in methylene chloride (40%), is placed in a flat sample cell (1.0 mm optical path) and illuminated by 295 nm u.v. light, there is no observable increase in the fluorescence emission. The same experiment, repeated using the solution squeezed between two slides separated by a $25\ \mu\text{m}$ Mylar gasket, does not show any emission increase either. In solution, the polymer molecules being formed are free to move away from the surface. Therefore, an absence of the signal increase indicates that when fast polymer-monomer exchange and mixing is possible throughout the solution, the mass balance of fluorescent molecules is maintained and the emission remains constant. In films, on the other hand, the polymer is formed due to monomer diffusion towards the illuminated surface and remains fixed in place by the binder used in the film. This absence of PVCA outflow from the illuminated region is responsible for the emission increase.

Changing the intensity of the excitation light changes the overall yield of the polymer (Figure 6a), but the normalized curves coincide, indicating that the polymerization is within the diffusion controlled limit (Figure

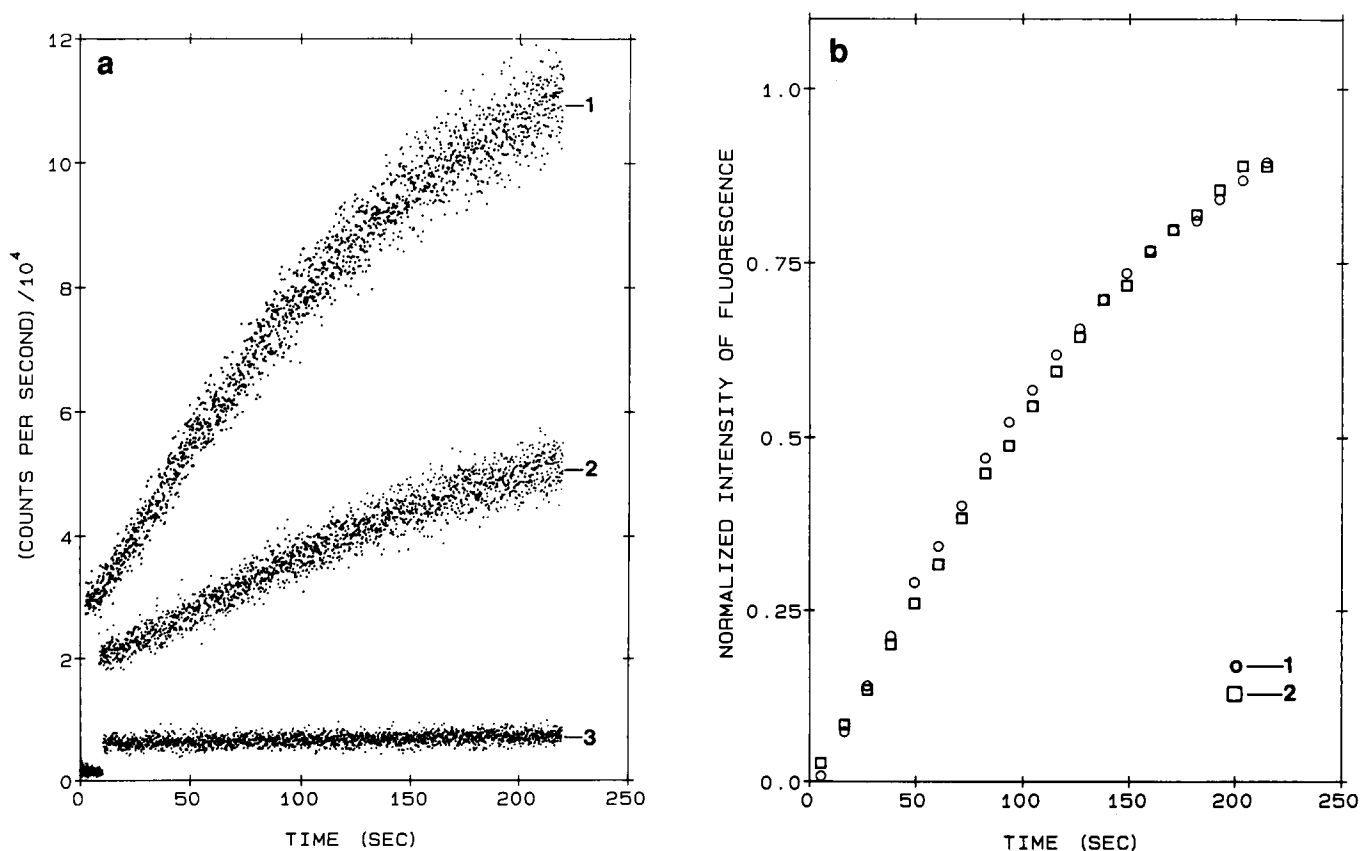


Figure 6 (a) Excitation intensity dependence of the fluorescence-detected photopolymerization kinetics with exposure at: 1, 100% intensity; 2, 75% intensity; 3, $\approx 20\%$ intensity. (b) The same kinetic data normalized to 1 (the 20% intensity data was omitted for clarity)

6b). Indeed, the higher intensity light produces a higher concentration of initiator radicals, yet the rate of their disappearance and polymer growth remains the same.

The light absorbance of the 20 μm film was ≈ 14 (recalculated from the absorption of the thinner film) (Figure 1) and, therefore, most of the light is absorbed in a layer at least one order of magnitude thinner than the film thickness. As a result, the polymerization reaction and fluorescence emission occurs primarily in the layer of the photopolymeric film which can be treated as infinitesimally thin relative to the film thickness.

Movement of the monomer molecules from the bulk of the photopolymeric film towards the illuminated surface with consequent monomer conversion to the polymer in an infinitesimally narrow region can be treated as analogous to the process of surface evaporation from a film or absorption on one of the film surfaces. Such a model is realistic considering that a large pool of polymeric radicals exists next to the film surface and that the rate of reaction of these radicals with the monomer molecules is much larger than the rate of monomer molecule approach. The 'absorption' process would stop only after the capacity of the absorbing surface is reached, the supply of the absorbant exhausted, or molecular equilibrium between the absorbing layers and the bulk of the film reached.

The increase in emitted fluorescence intensity after exposure of the back side of the film indicates that after the front side exposure some non-reacted monomer molecules remain in the bulk of the film. However, the same initial emission ($8.4 \times 10^4 \pm 200$ counts s^{-1}) is exhibited by the flip side of a 24 μm and a 39 μm thick film after equilibrium under illumination of the front surface is reached. Initial emission of the front surface is the same in both cases ($9.5 \times 10^4 \pm 200$ counts s^{-1}). The final emission was higher for thicker film ($(6.3 \pm 0.5) \times 10^5$ versus $(4.9 \pm 0.5) \times 10^5$ counts s^{-1}), suggesting that diffusion had stopped due to the establishment of some type of equilibrium in the bulk of the film rather than reaching the limiting density or viscosity of the photopolymer. The equilibrium is characterized by polymerization of $\approx 10\%$ of initial monomer. Investigation of the nature of this equilibrium lies outside the scope of this work.

To evaluate the diffusion coefficient of *N*-vinylcarbazole we selected films which are sufficiently thick to have an optical density > 10 at 295 nm, but thin enough to have negligible absorbance at 400 nm, corresponding to the region of fluorescence emission monitoring. Under such conditions the emission intensity is proportional to the number of carbazyl groups in the illuminated surface layer of the film. Casting of uniform 20–25 μm film without cracks and bubbles is most reproducible and, therefore, this thickness was selected for the controlled experiments and calculations.

Calculations

We monitored the emitted fluorescence where only the surface layer is exposed to the fluorescence excitation light. This is the layer where the polymerization is taking place. Consequently, we observe a signal change proportional to the amount of monomer leaving the bulk of the film and polymerizing.

The equation describing the loss of the diffusing substance by surface evaporation (this process is math-

ematically similar to the surface polymerization) is presented by Crank⁹ (p. 57), and is described below.

If the total amount of diffusing substance leaving the sheet up to time t is $M(t)$, then

$$\frac{M(t) - M(0)}{M(\infty) - M(0)} = 1 - \sum_{n=1}^{\infty} \frac{2L^2 \exp(-\beta_n^2 Dt/x^2)}{\beta_n^2(\beta_n^2 + L^2 + L)}$$

where: β_n are the positive roots of $\beta \tan \beta = L$; $L = x\alpha/D$; x is the film thickness in cm; D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), used as a parameter in the present calculations; and α is the proportionality constant, defined as the fraction of molecules at the surface that can evaporate. In the present model, every monomer molecule which has reached the illuminated surface polymerizes (evaporates from the bulk of the film). Therefore $\alpha = 1$. Under such conditions $L \rightarrow \infty$ and the equation can be approximated as:

$$\begin{aligned} [M(t) - M(0)]/[M(\infty) - M(0)] \\ = 1 - \sum_{n=1}^{\infty} \{2(\beta_n)^{-2} \exp(-\beta_n^2 Dt/x^2)\} \end{aligned}$$

The tabulated⁹ values of β_n for $L = \infty$ for up to $n = 6$ were used.

Due to complete absorption of the excitation light and essentially no attenuation of the fluorescence emission by the photopolymer film, the fluorescence intensity is proportional to the amount of monomer leaving the bulk of the film. Then the intensity ratio $[I(t) - I(0)]/[I(\infty) - I(0)]$ is considered equal to $[M(t) - M(0)]/[M(\infty) - M(0)]$. The calculated curves (with the diffusion coefficient used as a variable parameter) are superimposed on the experimental data (Figure 7). The diffusion coefficient

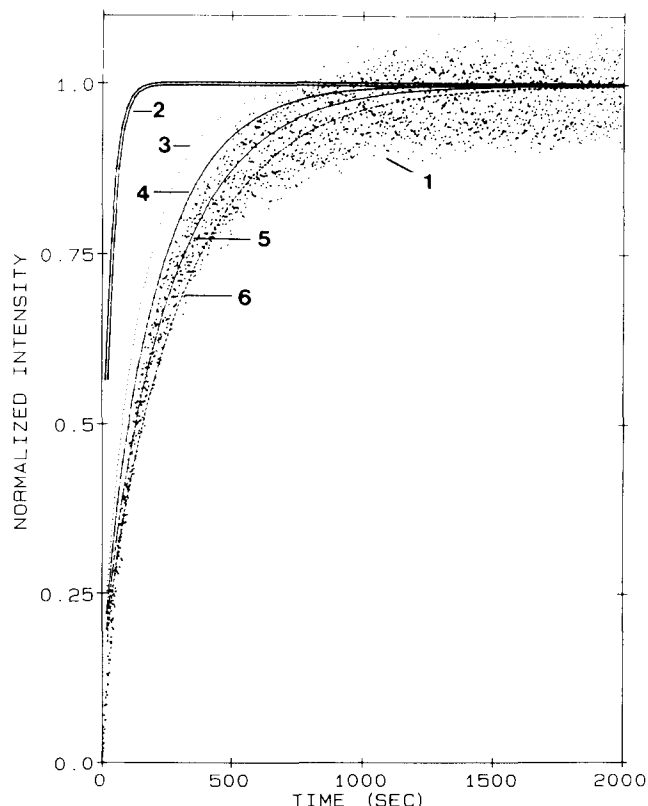


Figure 7 Experimental and computed data for photopolymerization kinetics in 20 μm film. The monomer diffusion coefficient was used as the adjustable parameter: 1, experimental data normalized to 1; 2, diffusion coefficient $5 \times 10^{-8} \text{cm}^2 \text{s}^{-1}$; 3, $1 \times 10^{-8} \text{cm}^2 \text{s}^{-1}$; 4, $7 \times 10^{-9} \text{cm}^2 \text{s}^{-1}$; 5, $6 \times 10^{-9} \text{cm}^2 \text{s}^{-1}$; 6, $5 \times 10^{-9} \text{cm}^2 \text{s}^{-1}$

giving the best overall fit to the data is taken as the diffusion coefficient of the *N*-vinylcarbazole monomer in the investigated photopolymer. Within the presented model the diffusion coefficient of *N*-vinylcarbazole at room temperature in the photopolymer is equal to $6 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$.

This diffusion coefficient is similar to the molecular diffusion coefficient in viscous fluids. This indicates that monomer migration and, consequently, the photopolymerization kinetics are controlled by the plasticizer viscosity rather than by the structure of the binder. Indeed there is no difference in the diffusion coefficient when the binder is changed from cellulose acetate to vinyl acetate. However, the reaction fails to proceed in the absence of a plasticizer. Further detailed investigations of the factors influencing the photopolymerization, such as viscosity of the plasticizer, mobility of the initiator, free volume of the binder etc. are currently being conducted to further elucidate the mechanism of the process.

CONCLUSION

We have measured polymerization kinetics and fluorescent monomer transport in photopolymerizable films using a direct and non-destructive method. This method is applicable to study monomer diffusion in a variety of existing photopolymers and photoresists. To the best of our knowledge these are the first such measurements to date.

The measurements determined that the rate of photopolymerization in photopolymer films is controlled by the rate of monomer diffusion towards the illuminated surface. Monomer (NVC) diffusion in vinylacetate binder occurred with the diffusion coefficient equal to $(6.0 \pm 0.5) \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, with the photopolymerization reaction proceeding until about 10% of the initial monomer present in the film was polymerized.

In our modelling of the photopolymerization process for the calculations, we tried to create a realistic picture and deduce a meaningful monomer diffusion coefficient. Most often, however, diffusion processes are treated using even simpler models requiring more severe approximations, thus forcing the use of only initial or final portions of the experimental curves¹⁰.

The technique developed requires straightforward equipment and does not need nanosecond time resolution like some methods of diffusion measurement based on fluorescence quenching.

We did not introduce fluorescent or radioactive tracers into the system and thus there was no perturbation of the photopolymer composition. Intensity of the excitation (analysing) light was maintained intentionally low to reduce the damage to the components of the photopolymer. In this respect this method offers advantages over methods based on fluorescence redistribution after pattern photobleaching, which apply a potentially damaging high power laser pulse to bleach the dye in the polymer before the kinetic measurements can start.

The main disadvantage of the diffusion measuring technique presented is its relatively narrow range of applications, restricted to photopolymers based on

fluorescent monomers. Nevertheless, a number of reactions could be studied, e.g. polymerization of vinyl-naphthalene and methylstyrene. Considering the widespread use of *N*-vinylcarbazole-based photopolymers in various photoimaging systems¹¹⁻¹⁹, the technique of polymerization kinetics monitoring described in this paper might find some interesting applications.

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