Kinetics of anisotropic photopolymerization in polymer matrix

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The photopolymerization mechanism is investigated in films consisting of a rigid plasticized polymeric matrix, photoinitiator and monomer. These photopolymers are widely used commercially in electronics, printing and holography. Illumination, typically from one side, initiates a chemical sequence that records the incident light pattern in the polymer. A method developed in our laboratory is employed to monitor the course of reaction. The photopolymerization rate and yield vary greatly with the distance from the film surface because of the high optical density of the film and the presence of oxygen. Monomer and oxygen migrate towards the illuminated surface of the film where most of the excitation and reagent consumption takes place. Thus the unidirectional illumination creates a spatially anisotropic distribution of reactants and products. A semiempirical computer model of the spatial dependence of photopolymerization kinetics is presented. Photopolymerization kinetics are studied as a function of film thickness, light intensity and rate of monomer diffusion. Calculations explain the experimentally observed kinetics and predict the time dependence of the polymer distribution in the film.

(Keywords: photopolymer; holographic polymer; polymerization; fluorescence; kinetics; computer modelling; anisotropy; diffusion)

INTRODUCTION

Photopolymerization is an extensively studied process[1] with an expanding commercial utility. A variety of printing and electronic applications are based on photopolymerizable formulations[2]. With rare exception all the processes are conducted while illuminating the sample from one side. Needless to say, the light has to be absorbed by the reactive molecules to initiate any chemical transformation and its intensity diminishes by absorption with distance from the surface, according to the Lambert–Beer Law. Since the intensity of excitation varies through the sample, the photochemical processes taking place are spatially inhomogeneous. Since in traditional organic and polymer chemistry the reactions are conducted in a stirred tank mode, only limited attention was devoted to the question of spatially inhomogeneous radical photopolymerization. The subject was addressed by Shultz[3] and Lissi[4] and their co-workers who gave detailed theoretical consideration of the kinetics of photopolymerization in well stirred and unstirred reactors illuminated unidirectionally. However, the kinetic equations were derived with assumptions of steady-state concentrations of radical species in the system and negligible depletion of photoinitiator. No assessment of influence of the diffusion rate of molecular species within the reaction zone was made and effects of possible impurities were ignored. In viscous unstirred media diffusion is an important rate-controlling process and cannot be omitted in modelling. The steady-state approximation for the transients is not necessarily valid either.

The question of anisotropic diffusion controlled photopolymerization reaction is reexamined here for the particular case of photopolymer films. Photopolymers can be defined as a class of photopolymerizable compositions consisting of a plasticized inert polymer matrix (binder) and dissolved photoinitiator, monomer, chain transfer agents and sensitizing dyes[2,5–7]. When the photopolymer film is illuminated by ultraviolet light, strongly absorbed by the organic molecules[8], the polymerization proceeds more rapidly near the illuminated surface of the film, creating a monomer concentration gradient, leading to monomer migration from the bulk of the film towards the illuminated surface. In plasticized polymer matrix the migration rate of polymer molecules is several orders of magnitude slower than that of the monomer. Therefore there is little or no outflow of forming polymer and it accumulates near the illuminated surface. In our experiments the monomer and polymer are fluorescent. Thus, the monomer migration and polymer accumulation in the illuminated region result in progressive increase in fluorescence intensity[6].

With recent development of high resolution microlithographic, photoresist, digital recording and holographic technologies based on photopolymerizable formulations[2,5,7], it became imperative to understand and manipulate the factors controlling the depth profile of the products resulting from photopolymerization. It is a special concern when the products are washed away and the shape of the remaining pit is important for further application[2,5]. Recently we developed and applied a fluorescence-based experimental technique to monitor kinetics of photopolymerization and accompanying monomer diffusion in photopolymer films[6]. In the present work we attempt to establish a realistic photopolymerization model qualitatively reproducing our experimental data and use this model to illustrate the peculiarities encountered in photopolymerization occurring in the films illuminated unidirectionally. We present a detailed

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experimental and theoretical analysis of the kinetics and mechanism of the photopolymerization process in the polymer matrix. Diffusion of reactive species towards the light is taken into account. Since in imaging applications the reaction is most often conducted in the presence of oxygen, the effects of oxygen on the mechanism and kinetics are also included. The experiments were conducted using Du Pont holographic photopolymer[7].

EXPERIMENTAL

Materials

Photopolymer film used in the experiments is based on a fluorescent monomer, *N*-vinylcarbazole (NVC) (Aldrich); *o*-chlorohexaphenyl-bi-imidazole (synthesized in this laboratory) is used as photoinitiator[2,7]. The photopolymer film is cast on a Suprasil quartz slide and in some experiments is sandwiched between two Suprasil slides. The resulting polymer, poly(*N*-vinylcarbazole) (PVCA) contains fluorescent carbazyl groups as side substituents on a polyvinyl back bone.

Apparatus and run procedure

The experimental set-up used for measurement of this change in concentration of fluorescent units is described in detail elsewhere[6]. It consists of a 150 W xenon arc light source for photoinitiation and fluorescence excitation. The excitation light is monochromated and filtered to obtain a relatively narrow band at 295 nm where both NVC and PVCA have equal extinction coefficients. The fluorescence signal is collected by a photomultiplier tube, amplified and processed by a conventional photon counter interfaced with a microcomputer for data collection and processing. NVC and PVCA have equal fluorescence yields around 400 nm. Therefore fluorescence is detected at wavelength 400 nm (monochromator, filters) in a transmission mode at ~45° angle relative to the direction of excitation light. The self-absorbance of the fluorescence by the sample at wavelength 400 nm is negligible[6]. Special care is taken to ensure that the intensity of u.v. light is low enough to avoid decomposition of monomer, resulting polymer and other components of the formulation.

COMPUTATIONAL MODEL

Kinetic model of photopolymerization

During photopolymerization, monomer is consumed due to the reaction near the surface of the film. The resulting monomer concentration gradient leads to monomer migration towards the illuminated surface. Polymer, on the other hand, is practically immobile in the matrix. Thus the total number of illuminated carbazyl groups (in NVC and PVCA) increases, and the intensity of fluorescence increases as well. This increase in fluorescence characterizes the kinetics of polymerization in photopolymer films. When the film is exposed from the opposite side, the initial fluorescence is lower due to the lower amount of monomer remaining. In the case of film exposed to air, the total increase in fluorescence intensity is lower as well (*Figure 1*)[6]. In the earlier work[6,9,10] the model based on the assumption of monomer 'evaporation' as it reacts near the surface was used to deduce the diffusion coefficient. It was assumed that the reaction occurs in an infinitesimally narrow region near the surface. In the present study we extend the detailed physical and chemical scheme of the process to the full thickness of the film.

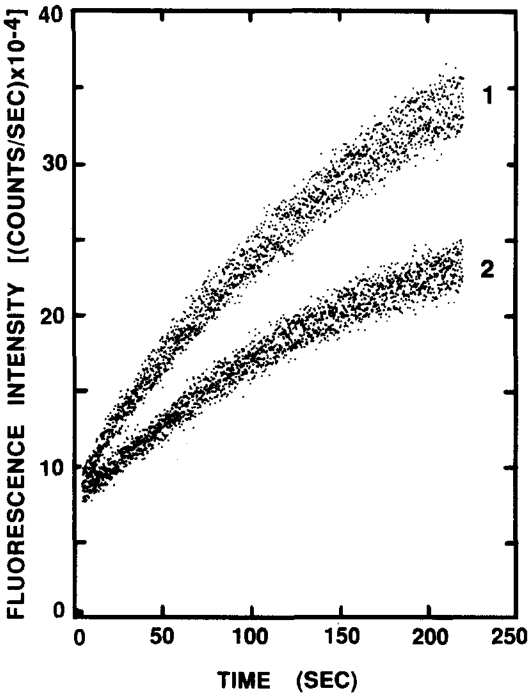

Figure 1 Change in the intensity of fluorescence emitted by the 24.5 μm photopolymer film illuminated first from its oxygen impermeable side (1) and then exposed from the flip side (2), open to air

A conventional free radical polymerization mechanism is adopted for the mathematics of the kinetic model[1].

$$S + h\nu \rightarrow S^* \rightarrow S\cdot$$
$$S\cdot + M \rightarrow M\cdot + \mathrm{Pr}$$
$$S\cdot + \mathrm{O}_2 \rightarrow S\mathrm{OO}\cdot$$
$$S\cdot + C \rightarrow C\cdot + S$$
$$M\cdot + M \rightarrow \mathrm{M}_2$$
$$M\cdot + \mathrm{O}_2 \rightarrow M\mathrm{OO}\cdot$$
$$M\cdot + M\cdot \rightarrow M_2$$
$$M\cdot + C \rightarrow C\cdot + M$$
$$\cdots\cdots\cdots\cdot$$
$$M_{k-1} + M \rightarrow M_k$$
$$M_{k-1} + M\cdot \rightarrow M_k$$
$$M_{k-1}\cdot + \mathrm{O}_2 \rightarrow M_k\mathrm{OO}\cdot$$
$$M_{\dot{k}} + C \rightarrow C\cdot + M_k$$

where S is photoinitiator, M is a monomer, $M_{\dot{k}}$ is a radical containing k monomeric units, and C is a chain transfer agent. The rate of polymer diffusion in a solid matrix is low, therefore the chain termination due to recombination of the high molecular weight radicals is a relatively slow process and is omitted from the kinetic scheme presented above.

Restrictions are imposed on some of the steps because of the limited mobility of large species in the non-stirred environment. Alternatively the mobility of small species by diffusion is emphasized for the important consequences in the mechanism that are observed in our experiments.

The concentration of monomer radicals is low and polymerization due to migration of the monomer radicals, $M\cdot$ out of the illuminated region was omitted from consideration as well. The size of the molecule of the photoinitiator used in photopolymer formulations is higher than that of M_3 and one can neglect its migration within the polymer matrix as well. In radical photopolymerization the initiation can also occur through the reaction:

$$S\cdot + M \rightarrow SM\cdot$$

which also yields relatively large slow moving molecules. Therefore the migration of initiator is omitted here.

Photoinitiation

Decomposition rate of the photoinitiator depends on its extinction coefficient, the local concentration and the local light intensity:

$$\partial[S]/\partial t = -\varepsilon_s[S]I \tag{1}$$

In the equation $[S]$ represents initiator concentration, I light intensity, ε the extinction coefficient of the initiator and t time. Diffusivity of the initiator molecule is assumed negligible. This assumption holds for large *o*-chlorohexaphenyl bi-imidazole molecules used as initiators in the present work.

Two radicals are generated for each molecule dissociated. It is assumed they immediately combine with monomer and they too are immobile. Initiator recombination is omitted in this environment due to the low radical concentration relative to that of monomer, chain transfer agent and oxygen. Therefore the initiation rate is:

$$(\text{Rate})_{\text{initiation}} = -2\{\partial[S]/\partial t\} \tag{2}$$

Propagation

The addition of monomer to radicals, whatever their length, is represented by the usual propagation rate expression:

$$(\text{Rate})_{\text{propagation}} = K_p[M]\left\{\sum_{j=1}^{\infty} r_j^*\right\} \tag{3}$$

In the equation K_p is the second order rate constant, [M] and r_j^* are the concentrations of monomer and radical of chain length j respectively. Provision for copolymerization has been tried but not reported here. Local monomer concentration is depleted by propagation but importantly it is supplemented by diffusion from adjoining regions richer in monomer. The rate of change in monomer concentration is represented by:

$$\partial[M]/\partial t = D_m\{\partial^2[M]/\partial z^2\} - K_p[M]\left\{\sum_{j=1}^{\infty} r_j^*\right\} \tag{4}$$

The monomer diffusivity, D_m, is included to account for the transport by molecular diffusion. The spatial variable, z, is a measure of normal distance below the film surface. There is no transport by convection and the turbulent convective homogenization of the stirred tank[3,4] does not pertain to the matrix medium of photopolymerization in films.

All monomer included in propagation ends up in polymer. The monomer may be present in suitably terminated chains or in active radicals but all are included in the polymer accounting. Neither polymer molecules nor polymer radicals migrate, consequently:

$$\partial[P]/\partial t = K_p[M]\left\{\sum_{j=1}^{\infty} r_j^*\right\} \tag{5}$$

where $[P]$ represents polymer concentration as equivalents of monomer converted in the polymerization.

Molecular weights and distribution are not a concern in this study, therefore chain transfer relative to initiation is omitted in the model. Undoubtedly there will be considerable differences in molecular weights in regions with intense initiation compared to regions where initiation is subdued.

Termination

The free radicals in the system are large and immobile with a small probability to terminate by recombination. They can survive for extended durations sustaining polymerization even in the dark and degenerating the fidelity of any image produced in exposure.

An alternative to recombination is scavenging by oxygen with the formation of intractable peroxy radicals and reaction with chain transfer agent, C. The chain transfer agent C is added in photopolymer formulations to ensure more uniform polymer chain length. Here, instead of considering the slowing of the polymerization reaction by chain transfer, we use a chain transfer agent as a weak chain-terminator, free to diffuse within the film:

$$(\text{Rate})_{\text{termination}} = \{K_T[O_2] + K_{CT}[C]\}\left\{\sum_{j=1}^{\infty} r_j^*\right\} \tag{6}$$

where K_T and K_{CT} are the second order rate constants of chain termination by O_2 and chain transfer agent, respectively. Oxygen is naturally absorbed from the air during the film casting and, in the case of uncovered film, even during light exposure. Its local concentration changes by the reactions of peroxide formation and diffusional restoration from the oxygen supply at the film boundaries (except when barrier films isolate air).

$$\partial[O_2]/\partial t = D_{O_2}\partial^2[O_2]/\partial z^2 - K_T[O_2]\left\{\sum_{j=1}^{\infty} r_j^*\right\} \tag{7}$$

The oxygen diffusivity, D_{O_2}, is larger than that of monomer. Oxygen concentration in equilibrium with air is quite small relative to initiator and monomer concentrations in the usual film recipes, else photopolymerization might never be successful.

Radicals

Free radical concentration varies in the film. Actual levels depend upon local rates of formation and termination:

$$\partial R^*/\partial t = 2(\partial S/\partial t) - \{K_T[O_2] + K_{CT}[C]\}\left\{\sum_{j=1}^{\infty} r_j^*\right\} \tag{8}$$

where

$$R^* = \sum_{j=1}^{\infty} r_j^*$$

Integration of equation (8) from an initial condition of no free radicals automatically includes any delay for scavenging oxygen by initiator before polymerization proceeds. This procedure avoids equating the rates to evaluate radical concentrations by algebra, the common approach when the stationary state hypothesis is invoked.

Local light intensity

Light can be absorbed by initiator, monomer, polymer and background species such as dyes, sensitizers and the binder in the film. Consequently local intensity depends on the extent of light absorption along the path from the surface. By reaction and diffusion, initiator and monomer–polymer concentrations change thereby altering the light intensity, but the effect may be insignificant since the optical density of all other absorbers is so large. Independence of the extinction coefficients of the separate species is assumed in writing the differential equation for the attenuation of intensity in the film:

$$\partial I/\partial z = -I\left\{\varepsilon_s[S] + \varepsilon_m([M] + [P]) + \sum_k (\varepsilon_k[Q]_k)\right\} \quad (9)$$

where $[Q]_k$ represents the concentration of the kth component of the mixture. The extinction coefficient of the polymer in this model is equal to that of the monomer since that is the case for NVC and PVCA at 295 nm[11].

Fluorescence intensity

We observe experimentally a fluorescence emitted by a sample as a function of time of illumination (*Figure 1*). In a simplified mathematical treatment of the data presented in earlier work[6] we considered fluorescence roughly proportional to the concentration of the fluorescent species. A more comprehensive treatment is used in the present work. The fluorescence intensity is proportional to the amount of light absorbed by the fluorescent groups. The monomer radicals do not fluoresce due to a substantial intramolecular quenching[7]; however, dimeric and higher molecular weight radicals are treated here as fluorescent species. The spatial derivative of the fluorescence intensity is given by:

$$\partial(I)_{\text{fluorescence}}/\partial z = Iqf\varepsilon_m([M] + [P]) \quad (10)$$

where q is an average quantum yield and ε_m is an average extinction coefficient of carbazyl groups in monomer and polymer. The factor f is a parameter designed to account for the presence of fluorescence quenchers in photopolymer formulations. Integration of equation (10) over the film thickness gives the intensity of fluorescence. In the photopolymer formulation studied there are some fluorescence quenchers, such as compounds containing heavy atoms, dissolved in the polymer matrix. As photopolymerization occurs and monomer starts migrating towards the illuminated surface, local concentration of fluorescent groups increases and the ratio of concentrations of illuminated fluorofore to quencher increases as well. Thus a quantum yield of fluorescence changes in the course of photopolymerization. Therefore two factors lead to the increase in fluorescence intensity: (1) the increasing number of illuminated fluorescent groups; and (2) the increasing yield of fluorescence. According to Stern-Volmer law a fluorescence quantum yield is inversely proportional to the fluorescence quencher concentration[8]. We combined the two effects in a single parameter, f, equal to the fluorofore fraction in a fluorofore-quencher mix and included f in equation (10). The factor f is coordinate-dependent and adjusts the fluorescence quantum yield to the change in relative quencher concentration.

Equation (10) provides the basis for linking the experiments and model by comparing the observed and computed fluorescence intensities. If the approximate physical model presented above is reasonable, the calculated and observed dependence of fluorescence intensities on the time of illumination will change similarly when reaction conditions are modified.

Calculation parameters

The mathematical model of photopolymerization contains many parameters including:

1 kinetic rate constants for chain propagation and termination by oxygen;
2 diffusivities of monomer and oxygen in the matrix;
3 extinction coefficients of initiator, monomer and background components;
4 equilibrium atmospheric absorption of oxygen;
5 operating variables of film thickness, incident light intensity and initial concentrations of initiator and monomer; and
6 essential physical constants of quantum yield and quenching efficiency for fluorescence.

A few are known, some can be estimated and others identified for determination in supplementary experimental studies.

Values for all the parameters are selected based on the existing experimental data obtained in this laboratory and from the literature. The set naturally includes the thickness (24.5 μm) and recipe concentrations of monomer (8 wt%), chain transfer agent (2.3 wt%) and initiator (2 wt%) used in the experiments. An equilibrium oxygen level of 90 ppm (3×10^{-6} mol cm^{-3}) was assumed typical of oxygen concentrations in viscous organic liquids exposed to air at room temperature[12]. Rate constants of 1.2×10^{10} cm^3 mol^{-1} s^{-1} for chain propagation and 1.5×10^{11} cm^3 mol^{-1} s^{-1} for oxygen scavenging were employed based on similar values in the literature for a wide variety of polymerization systems[13,14].

A more complicated situation exists with the choice of diffusion coefficients of monomer and oxygen. Diffusion coefficients are not measured directly but are deduced from experimental data using a variety of mathematical models and approximations. We use a value of the oxygen diffusion coefficient evaluated from data on oxygen induced quenching in a similar polymer matrix[15]. That value of the diffusivity is approximately 10^{-7} cm^2 s^{-1}. The monomer diffusivity was deduced earlier[6] to be 6×10^{-9} cm^2 s^{-1}. To determine the diffusion coefficient with more certainty, concentration profiles have to be observed. This is impossible with the geometry of a thin film but in the case of diffusion within the plane of the film, fluorescence-based methods yield good visual data[16].

The extinction coefficient for the NVC and PVCA is equal to 3×10^7 cm^3 mol^{-1} cm^{-1} at 295 nm[11]. Several values for intensity of the excitation light are used, all around 2.5×10^{-8} (mol photons) cm^{-2} s^{-1}.

Initial and boundary conditions

Initially all the ingredients are uniformly distributed according to the recipe of formulation. This includes oxygen since the manufacturing of photopolymer films does not exclude air.

It is assumed that all ingredients except oxygen (in the case of no covers) are confined to the film and hence gradients vanish at the surfaces, an essential condition in the absence of mass transfer at boundaries. The oxygen gradient vanishes at the surface in the presence of an impermeable barrier layer. Alternatively the oxygen concentration is constant at its atmospheric equilibrium level. It is not possible to have both surfaces exposed to air with the very thin photopolymer films. A base or supporting layer is necessary on one side for mechanical integrity.

The incident light beam has a fixed intensity. Experimentally the sample can be illuminated from both sides by flipping the film sandwiched between the two slides (*Figure 1*). Incidence of the light beam in the model can be step turned by 180° at a prescribed time for imaging on the 'flip' side.

Calculations

The geometry of the problem lends itself to a finite difference approach in simultaneous solution of the partial differential equations by the method of points. The thickness of the film is non-uniformly discretized with the smallest intervals near the surface in the vicinity of anticipated abrupt and rapid changes. Partial derivatives in the geometric variable, z, are approximated by three-point formulas with unequal intervals. The number of divisions in discretization is optional but computed results show 25 divisions give good accuracy at reasonable computing times. More points may be needed under extreme conditions; this need becomes self-evident in examination of the results. The discretization between surfaces is symmetric about the midplane for ease in processing flip side exposures.

Time derivatives of all the dependent variables are integrated by a stiff differential equation solver (Gear). Elements in the Jacobian are evaluated by numerical differencing. Results are recorded at selected fractional times of the overall exposure period. The results may be printed but most often are plotted due to the overwhelming preference for the power of graphics in communication.

RESULTS AND DISCUSSION

Verification of the model

Our method for monitoring photopolymerization kinetics is based entirely on the detection of the fluorescence emitted by the film. To verify our proposed kinetic model we use it to compute the fluorescence intensity for comparison. No assumptions are made concerning the thickness of fluorescing layer, constant optical density etc. as was done previously[3,4].

The experimental data presented below are collected using the photopolymer films cast between two quartz slides to ensure that both surfaces are optically equivalent[6]. The film is spin-coated on one slide, the small square (5 x 5 mm) is carved out of it and the polymer outside the square boundaries is removed. Then the film free of solvent is covered by another slide[6]. The film is imaged first from the spin-coated side. The oxygen flow from the flip side of the film and from the boundaries is not restricted. This ensures roughly the same oxygen concentration before and after the front surface exposure. The increase in fluorescence intensity resulting from photopolymerization at the surface and concurrent monomer migration is presented in *Figure 1*. After the fluorescence increase stops, the flip side of the film is exposed. This exposure produces lower initial fluorescence intensity and lower increase in fluorescence intensity over the time of exposure, than that of the front side. This, of course, occurs because some monomer is already consumed and diffused away during exposure of the front surface. The fluorescence intensity growth resulting from the sequential exposure of the front and flip sides of the film with an oxygen barrier only on the front side (*Figure 1*) is qualitatively reproduced by the model calculations (*Figure 2*). Variation in the monomer diffusion coefficient in the model causes substantial change in the calculated increase in fluorescence intensity (*Figure 3*).

Using the model to deduce the diffusion coefficients, one has to take into account that variation of other kinetic and transport parameters described below can alter the deduced values of monomer diffusion coefficients as well. We do not have exact values of many parameters in the model, so we intentionally do not try to match the experimental and computed data by varying the monomer diffusion coefficient, as was done in refs 6, 9 and 10, but simply use the value of ref. 6. This value is similar to the value reported by other researchers[17]. The increase in fluorescence intensity calculated using the monomer diffusion coefficient reported earlier is roughly of the same order as the experimental one. The results satisfy the goal of these studies to demonstrate the main principles and peculiarities of the unidirectional exposure, rather than to deduce the physical constants.

The increase in fluorescence intensity depends on the thickness of the film. The 24.5 and 39.2 μm films exhibit different behaviour (*Figure 4*), although the photoexcitation is limited to the same relatively narrow layer near the surface of the film ($<1\ \mu$m). The kinetics are dependent on thickness because in thicker films larger amounts of monomer are available in reserve to diffuse towards the front surface during reaction. However, the amount of initiator in a photoactive layer is limited, since make-up by the immobile initiator is not possible. As a

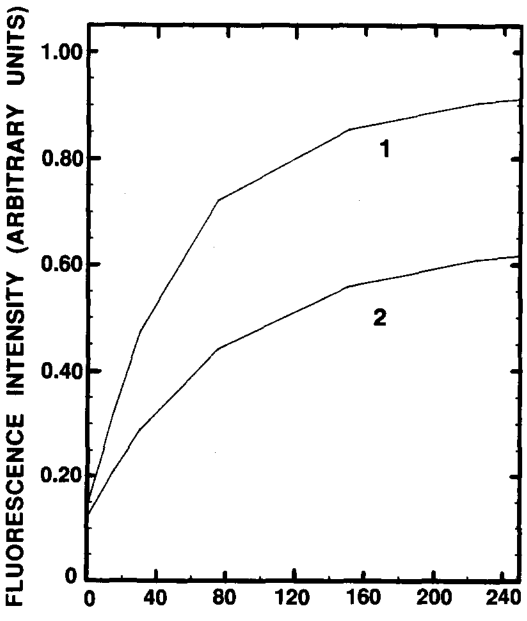

Figure 2 Model calculations of the fluorescence detected kinetics of photopolymerization occurring in consecutive two-sided u.v.-exposure of the 24.5 μm photopolymer film: 1, front (oxygen impermeable) surface exposure; 2, flip (unprotected) side exposure

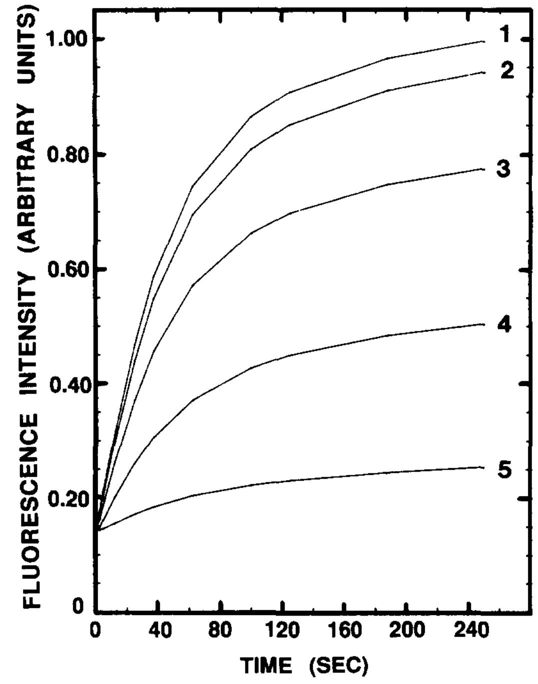

Figure 3 Model calculations of the effects of the change in the monomer diffusion coefficient on fluorescence detected photopolymerization in 24.5 μm film in contact with air on the unexposed side. Diffusion coefficient (cm^2 s^{-1}) varies from curve to curve as: 1, 10^{-7}; 2, 10^{-8}; 3, 10^{-9}; 4, 10^{-10}; 5, 10^{-11}

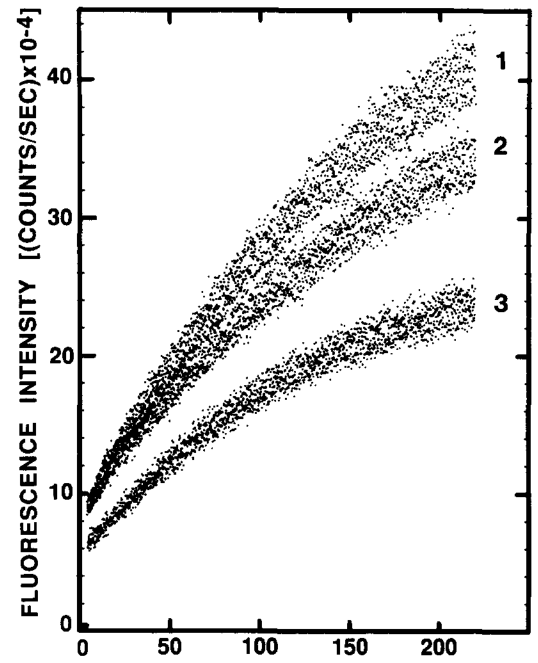

Figure 4 Experimental film thickness dependence of the fluorescence detected photopolymerization kinetics: 1, 39.2 μm film; 2, 24.5 μm film; 3, 0.7 μm film. Front surface is illuminated, the flip surface is exposed to air

result, at large film thickness, increase in thickness does not produce further increase in polymer yield. Thicker films can act as oxygen barriers and at large thickness there is little difference between the film isolated from the air and that exposed to the air from the flip side. The calculations reproduce the experimentally observed trend (*Figure 5*).

The kinetics of photopolymerization depend strongly on the intensity of the excitation light. Experimental dependence of the fluorescence intensity on time of exposure at different intensities is presented in *Figure 6*. The model calculations predict similar behaviour (*Figure 7*). Higher light intensity results in higher rates of initiation and polymerization. Changes in local light intensity are included in the model by differential equations for the effects of elapsed time, loss of initiator and light absorption below the surface. Therefore we do not deduce the analytic expression for the dependence of photopolymerization rate on the light intensity, as was done in early studies of photopolymerization kinetics[1].

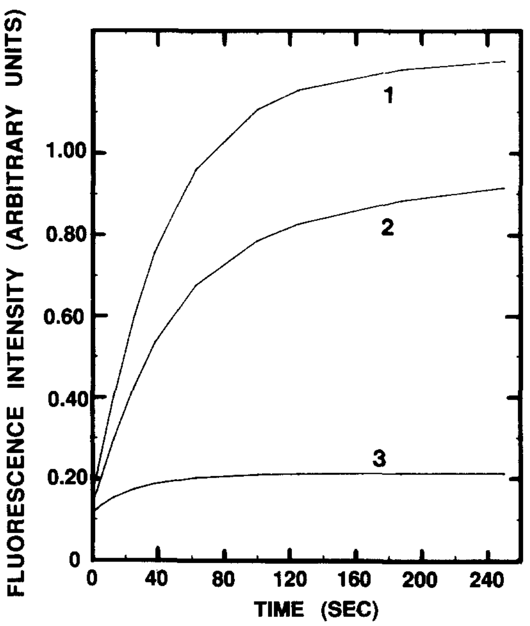

Figure 5 Calculated thickness dependence of the photopolymerization kinetics in photopolymer in contact with air on the unexposed side: 1, 39.2 μm film; 2, 24.5 μm film; 3, 0.7 μm film

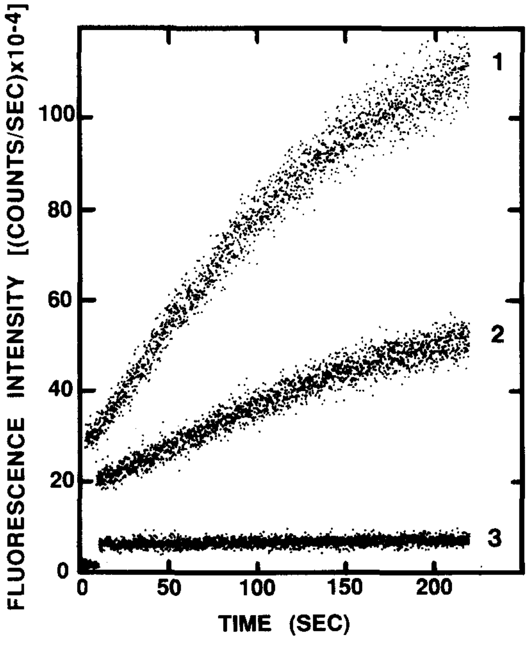

Figure 6 The experimental intensity dependence of the photopolymerization kinetics in photopolymer film in contact with air on the unexposed side: 1, 100%; 2, 75%; 3, 10% of the initial light intensity

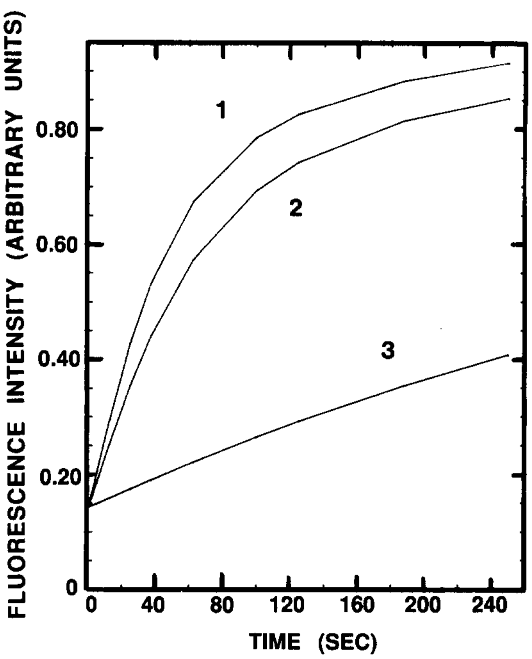

Figure 7 Intensity dependence of the photopolymerization kinetics in photopolymer film in contact with air on the unexposed side: 1, 100%; 2, 75%; 3, 10% of the initial light intensity

Calculated fluorescence reproduces the observed fluorescence qualitatively, supporting the assumption that the model reasonably approximates real processes occurring within the photopolymer film. It is used below to compute the time dependence of the product distribution in photopolymer during imaging. To the best of our knowledge there is no reported experimental data on product distribution profiles within films with thickness on the order of several micrometres. The absence of experimental data makes the computations particularly useful in the case of thin photopolymer films of commercial use.

Anisotropic photopolymerization

Since the computational results qualitatively reproduce the experimental data we use the kinetic model described above to elucidate those variables in our anisotropic photochemical system which cannot be easily observed experimentally.

Computer simulations of the behaviour of the reactants, transient species and the products in the photopolymerization reaction are conducted using the kinetic model presented above. The distribution of the molecular species as a function of distance from the illuminated surface of the film is computed at different times from the beginning of irradiation. Spatial distribution of the polymer is of particular practical interest since the quality of holograms, electronic circuits and printing plates depends greatly on its homogeneity. In most printing and electronic applications the photopolymer film is isolated from atmospheric oxygen by impermeable polymer covers. The detailed investigation of oxygen effects on photopolymerization kinetics is outside the scope of this paper. Therefore in further discussion we consider only film isolated from oxygen uptake during imaging. Work on oxygen effects on photopolymerization in dry films is currently in progress and some preliminary results have been reported[9,10].

The light comes from one direction, therefore the products are not distributed isotropically. As expected, the initiator consumption is strongest at or near the photopolymer film surface (*Figure 8*). The radical concentration and distribution in film depends on the excitation light and concentration of initiator, oxygen and chain-transfer agent. The maximum concentration of radicals is much lower than that of other species and is in the order of 10^{-14} M. Initiator, as well as radicals, is reacting near the illuminated surface and portions of the film farther from the illuminated surface are not involved. However, the species which are mobile in the matrix such as oxygen, chain-transfer agent and monomer behave differently.

Oxygen and monomer molecules, like initiator, are consumed more rapidly near the illuminated surface. However, oxygen and monomer molecules are free to diffuse. Even though no reactions occur deep below the illuminated surface, oxygen and monomer are depleted by diffusion into the photoactive region (*Figures 9* and *10* respectively). At short times the change in monomer concentration from the illuminated surface is small. However, as polymerization continues, oxygen (film has impermeable boundaries) and monomer get distributed evenly through the film thickness. The monomer is consumed near the surface, but the 'information' about it propagates through the photopolymer with a delay stipulated by the monomer diffusion coefficient (*Figure 10*). Since the oxygen diffusion coefficient is higher, the uniformity of oxygen concentration is reached long before that of monomer. Oxygen is consumed faster, while most of the monomer and illuminated initiator are still available for the reaction (*Figures 9* and *10* respectively).

Chain transfer agent consumption dynamics closely resembles those of oxygen in the case of impermeable boundaries.

The differences in diffusion rates and concentrations of oxygen and monomer are responsible for the rather unexpected distribution of the forming polymer. Most of the polymer is formed near the illuminated surface within 10% of the film thickness, under our reaction conditions.

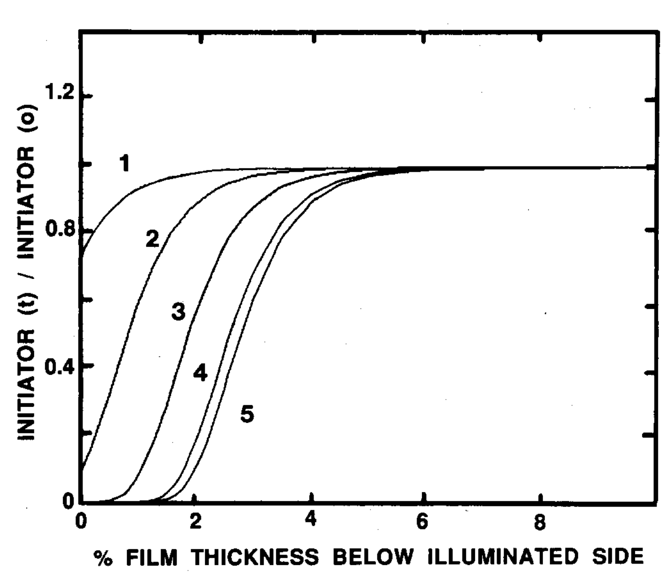

Figure 8 Initiator consumption during photopolymerization as a function of the distance from the illuminated film surface at times: 1, 13 s; 2, 100 s; 3, 500 s; 4, 1500 s; 5, 2000 s from beginning of exposure. Both surfaces are isolated from air

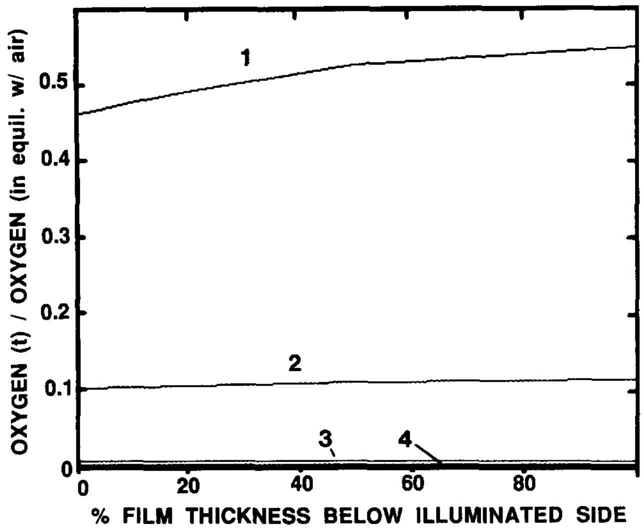

Figure 9 Oxygen consumption during photopolymerization as a function of the distance from the illuminated film surface at times: 1, 100 s; 2, 500 s; 3, 1500 s; 4, 2000 s from beginning of exposure. Both surfaces are isolated from air

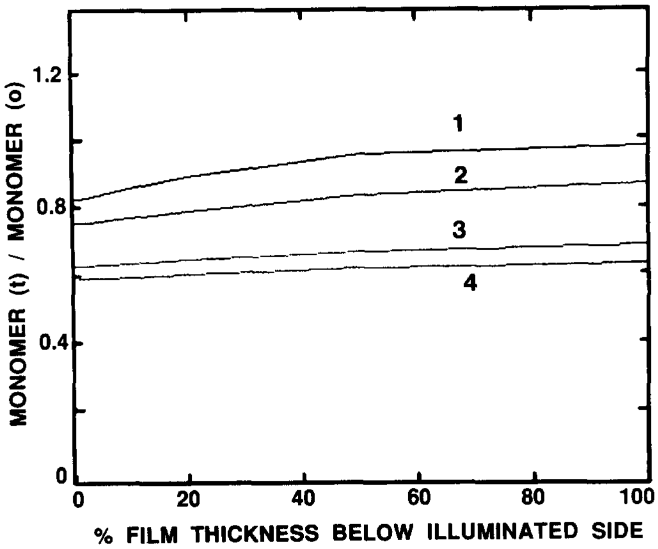

Figure 10 Monomer consumption during photopolymerization as a function of the distance from the illuminated film surface at times: 1, 100 2; 2, 500 s; 3, 1500 s; 4, 2000 s from beginning of exposure. Both surfaces are isolated from air

At long times much polymer is produced, not immediately under the surface, but some distance away from it (*Figure 11*). Apparently, this occurs in the region where oxygen concentration is depleted by the reaction with radicals, but enough light penetrates in to initiate the photopolymerization. In the course of reaction, as more oxygen is consumed, the maximum in polymer yield shifts even further away from the surface. The possibility of this anomaly has to be taken into account in holographic imaging where film of about 25 μm thick is imaged with the requirements of high uniformity[2,7]. The inhomogeneity is greatly reduced if the imaging is done at a wavelength at which the optical density of the material is low. Holographic images are produced in most cases using the longer wavelength irradiation; however, the film is covered by impermeable barriers on both sides[2,7] opening the door for inhomogeneity.

Reduction in the optical density of the film (by using light of longer wavelength) does not eliminate the anisotropy in polymer distribution, but shifts the polymer concentration maximum deeper into the film away from the illuminated surface. In the case of printing applications of various photopolymers, the inhomogeneous imaging can lead to uneven washout of the materials and loss in quality of the surface in microlithography. The calculations demonstrate that the uneven distribution of the forming polymer can be reduced by increasing the chain-transfer agent concentration or opening the film to oxygen flow. Preliminary calculations for the case of free oxygen access from the flip side of the film indicate that although the polymer is still formed near the illuminated surface, its spatial distribution is much more uniform. Further work on the connection of oxygen with uniformity of imaging is in progress[9,10].

When polymerization is complete or nearly complete, the product distribution remains uneven. In real photopolymer systems, the polymer and initiator also diffuse, although much more slowly than the monomer. However, the rate of the polymer chain migration is around two orders of magnitude lower than that of the monomer and the qualitative picture presented above is valid. Increasing the initiator mobility modifies the results, by compensating for lost initiator radicals near the surface. In the case of mobile initiator the maximum of polymer formation must shift to the illuminated surface. Some preliminary data on the effects of the initiator mobility have been recently reported[10].

CONCLUSION

We have considered photopolymerization in a film illuminated from one direction and presented a kinetic model which takes into account light attenuation by the media and resulting diffusion of the reactants towards the illuminated surface of the film where most of the polymerization occurs. No assumptions of steady state for the transient species were made. The calculated results qualitatively reproduce the observed experimental data. The calculations support our previous conclusion[6] that the increase in fluorescence intensity observed during

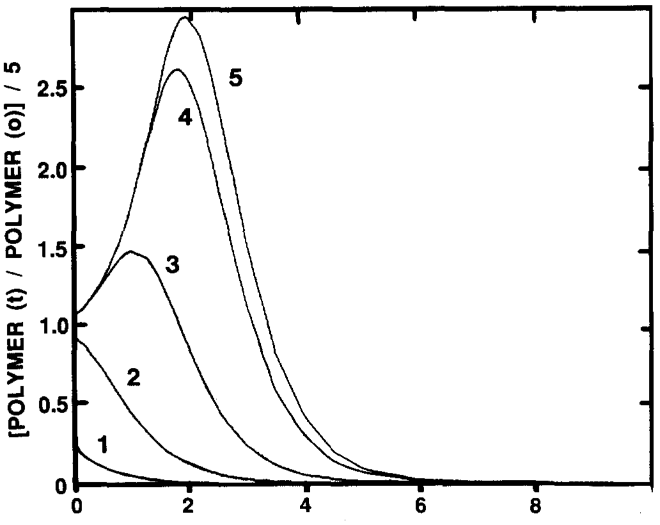

Figure 11 Polymer formation during photopolymerization as a function of the distance from the illuminated film surface at times: 1, 13 s; 2, 100 s; 3, 500 s; 4, 1500 s; 5, 2000 s. Both surfaces are isolated from air

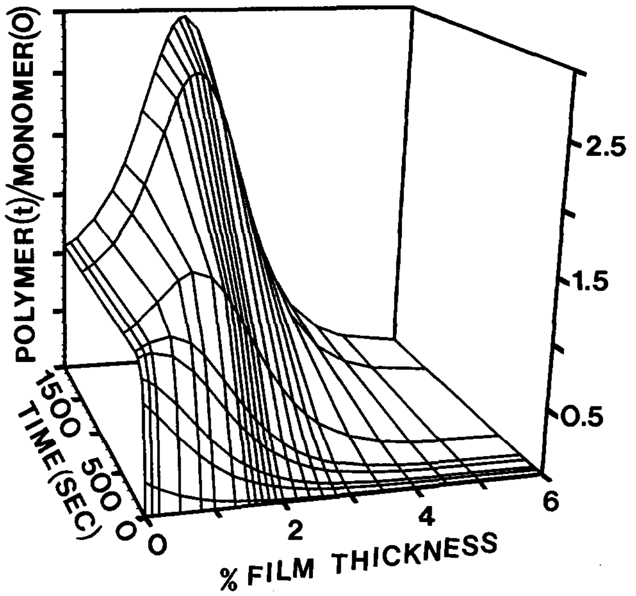

Figure 12 Three-dimensional diagram of the anisotropic formation of polymer during the photopolymerization in a film protected from air on both surfaces

photopolymerization of fluorescent monomer is connected with anisotropy of illumination, the resulting diffusion of monomer and the absence of polymer back-diffusion.

A possibility of a rather peculiar spatial distribution of products is computed. The spatial anisotropy of excitation light in the media and immobility of forming polymer chains and photoinitiator lead to polymer formation within 10% of the film thickness and at some distance from the illuminated surface (*Figures 11* and *12*).

Model calculations allow visualization of mutual dependence of many factors (not considered here in detail) such as excitation light intensity and oxygen effects as well as anisotropy of polymer formation. More detailed modelling of the effects of oxygen and variation in mobility of photoinitiator are now in progress. The diffusion coefficients for the monomer can be deduced from our experimental and calculated data provided that other parameters, such as the light intensity and oxygen migration rates, are known. Using proper experimental data, improvements in imaging can be made based on the model calculations presented above. The practical impact of the modelling of photopolymerization kinetics can be particularly high in the newly emerging area of three-dimensional imaging, dealing with highly anisotropic diffusion controlled processes[18].

Since photopolymerization in viscous media has a wide industrial application, we hope that this work will help to revive some interest to the unexpected problems which might occur in anisotropically activated photosystems such as photoresists, printing materials and holographic photopolymers.

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