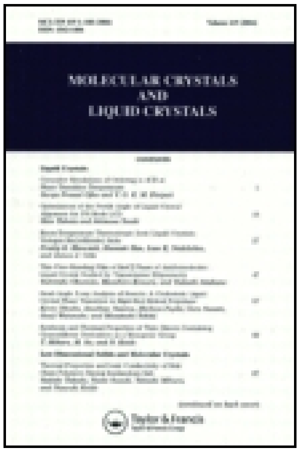

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Kinetics of Photopolymerization in Polymer Matrix

Vadim V. Krongauz [a] & Robert M. Yohannan [a]

[a] E. I. DuPont de Nemours & Company (INC.), Imaging Systems Department, Experimental Station Laboratory, Box 80352, Wilmington, DE, 19880-0352, U.S.A.

Version of record first published: 04 Oct 2006.

To cite this article: Vadim V. Krongauz & Robert M. Yohannan (1990): Kinetics of Photopolymerization in Polymer Matrix, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 183:1, 495-503

To link to this article: http://dx.doi.org/10.1080/15421409008047489

Mol. Cryst. Liq. Cryst., 1990, vol. 183, pp. 495–503
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

KINETICS OF PHOTOPOLYMERIZATION IN POLYMER MATRIX

VADIM V. KRONGAUZ* **AND ROBERT M. YOHANNAN**
E. I. DuPont de Nemours & Company (INC.), Imaging Systems Department, Experimental Station Laboratory, Box 80352, Wilmington, DE 19880-0352, U.S.A.

Abstract Photopolymers are widely used in the electronic and printing industries. These materials usually consist of a plastisized polymer matrix, photoinitiator, monomer and a variety of chain transfer agents. Photopolymerization in such systems is an interesting process but difficult to monitor. To facilitate the development of the new photopolymers a method for **direct** and **nondestructive** monitoring of reaction kinetics and monomer transport in photopolymers during photopolymerization was developed and applied. A change in the intensity of the fluorescence emitted by the photopolymer film containing the fluorescent monomer, N-vinylcarbazole, is used to monitor the photopolymerization process. The mechanism of inhomogeneous polymerization in photopolymers is discussed.

INTRODUCTION

The materials called "photopolymers" are widely used in electronic and printing industries. These materials consist of a plastisized polymer matrix, photoinitiator, monomer and a variety of chain transfer agents[1]. The exposure of the photopolymers to light initiates polymerization in the exposed regions, thus differentiating these regions from the unexposed areas. The use of photopolymers is expanding, encompassing areas of data storage and processing. A variety of new compositions are being sought to cater to these new applications. Development of new, more sophisticated materials requires a better understanding of the mechanism of operation of the existing systems, and that is the reason for undertaking the present study of photopolymerization kinetics in photopolymer films.

The photopolymers are most frequently used in a form of film coatings. Photopolymerization in such systems is difficult to monitor, since only small areas of the film are illuminated, and the amounts of products are minute and nonuniformly distributed[1]. The chromatographic techniques yield the results only after the reaction is complete and provide the information which is averaged through the imaged area. To the best of our knowledge, no fluorescent or isotope-labeling methods were applied to the investigation of kinetics of reactions in photopolymer films. The pattern photobleaching techniques[2] used to measure the diffusion within thin films demand a high intensity light which is damaging to the polymeric system and also were not applied for kinetic measurements. Holographic methods can be used to monitor the imaging kinetics[3,4] however the correlation of such data with the properties of the photopolymer and diffusion of the monomers is complicated and has not been done. To facilitate the development of the new photopolymers, we have developed a **nondestructive** method allowing **real-time** monitoring of the kinetics of photopolymerization in a film during the photoimaging.

To produce high quality printing plates, holograms and printed circuits the polymerization has to be uniform throughout the thickness of the film. However, the imaging light falls on the film from one direction and is attenuated by the photopolymer film. In optically dense films this leads to inhomogeniuty in polymerization. The focal point of our approach is the utilization of factors which, under ordinary industrial use of the photopolymers, present a problem: we acknowledged the nonuniform illumination of the film as a driving force for the diffusion of the reactive species and used it to our advantage.

EXPERIMENTAL

Materials Photopolymers used in this work were based on a fluorescent monomer, N-vinylcarbazole (NVC) dispersed in a plastisized Vinylacetate or Cellulose acetate matrix. Poly(N-vinylcarbazole) (PVCA) (Aldrich) was used for for some fluorescence measurements. The photopolymer films were spin or knife coated on quartz slides[5].

Method A change in the intensity of the fluorescence emitted by the plastisized vinylacetate film containing the fluorescent monomer, NVC, is utilized to monitor the photopolymerization process. The photopolymer film used in the experiments has a high optical density at the excitation wavelength (295 nm): more than 0.5 even for 0.7 μm film. We used films up to 50 μm thick. Due to the high optical density of the studied film the illumination of one side of the film leads to polymerization of the dispersed monomer and a reduction of its concentration predominately near the illuminated surface. This inhomogeneous polymerization gives rise to a monomer concentration gradient, and in the course of the reaction the monomer diffuses away from the bulk of the film towards the illuminated surface. The monomer and the resulting polymer contain fluorescent carbazyl groups. As their concentration near the illuminated surface increases, more and more fluorescent carbazyl groups are illuminated, thereby increasing intensity of the fluorescence emitted by the film. This increase in fluorescence intensity is used to monitor the kinetics of photopolymerization in a film (Figure 1)[5]. The fluorescence yields of NVC and PVCA are almost identical at 400 nm, thus this wavelength was chosen for the detection. The photopolymer film was squeezed between the two quartz plates to ensure that both surfaces of the film were equivalent. The entire area of the film was uniformly illuminated.

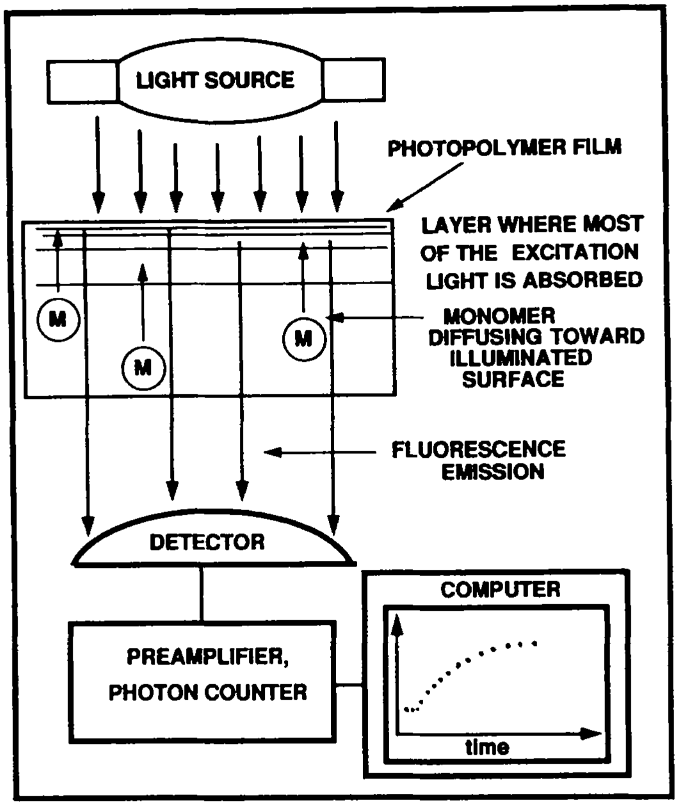

FIGURE 1 Schematic diagram of experimental set-up

The photopolymer film was placed at a 45° angle to the incident light and the detection was conducted perpendicular to the incident light using a conventional photon counting set-up. The scattered light was cut off using a series of filters and a monochromator in front of the phototube. A more detailed description of the materials and experimental procedures is given elsewhere[5]. The intensity of fluorescence increases dramatically in the course of the reaction (Figure 2). After one side of the film was exposed and the signal reached its limiting value the film was flipped over and illuminated from the other side. The decrease in the initial fluorescence signal from the flip surface indicates that the amount of monomer in the film is reduced by the initial exposure (Figure 2). The extent of fluorescence intensity increase due to the polymerization of the flip surface is also lower since less free monomer remains in the film after the front surface exposure. These results demonstrate that the monomer migration does take place during the exposure of the front surface.

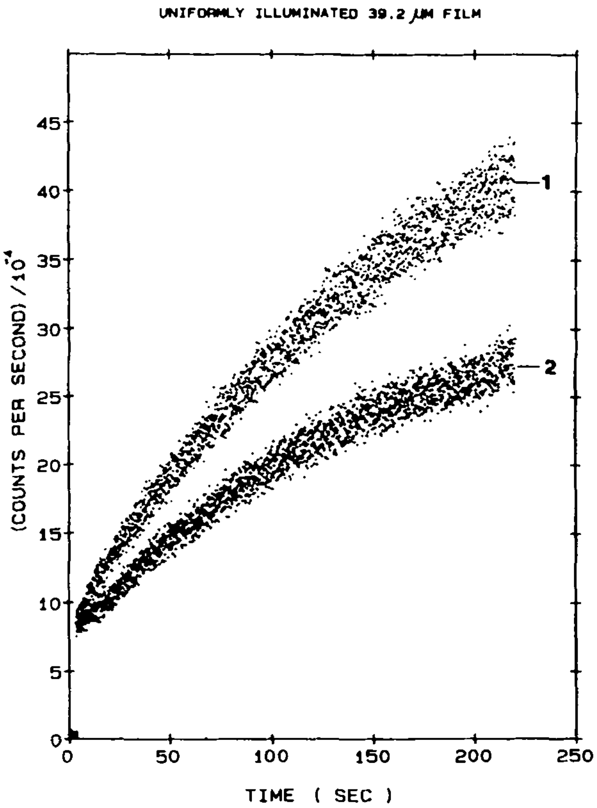

FIGURE 2 Time dependence of fluorescence intensity
1- Front surface exposure; 2- Flip surface exposure

RESULTS AND DISCUSSION

The rate of polymerization in a plastisized polymer matrix is controlled by the the rate of monomer diffusion[5,6]. A few simplifying assumptions about the photopolymerization process can be made to construct a realistic math model for calculation of the diffusion coefficient for the monomer. This process can be treated as if the reaction occurs in an infinitely thin layer near the surface and each carbazyl group we observe is already converted into a polymer or a polymer radical since it has seen the light. One can also neglect the chain propagation into the dark region due to the migration of the radicals away from the illuminated surface.

When these assumptions are made the process of this "unidirectional" photopolymerization can be treated mathematically in analogy to the process of evaporation: coming to the illuminated region the monomer "evaporates" from the bulk of the film. This treatment is particularly valid for thicker films with higher optical density, since in that case the depth of the light penetration is small relative to the thickness. We accepted the solution of the problem of evaporation from the infinite sheet as a basis for calculating the diffusion coefficient[7]. The results of these calculations using a diffusion coefficient as a parameter are compared with the experimental data for 20µm film with the optical density of 14 (Figure 3). The best fit to the data is obtained when the monomer diffusion coefficient, $D = 6\times10^{-9}$ cm^2/sec, is used.

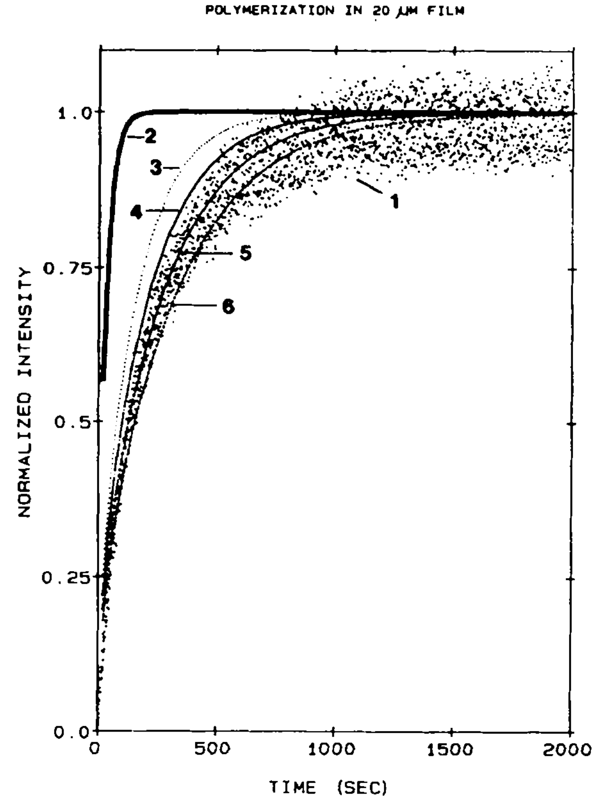

FIGURE 3 1- Experimental data normalized to 1; Computations with following diffusion coefficients (cm^2/sec): 2- 5×10^{-8}, 3- 1×10^{-8}, 4- 7×10^{-9}, 5- 6×10^{-9}, 6- 5×10^{-9}

Since the photopolymerization kinetics here is diffusion controlled, it varies substantially with the polymer matrix used in the photopolymer formulation (Figure 4).

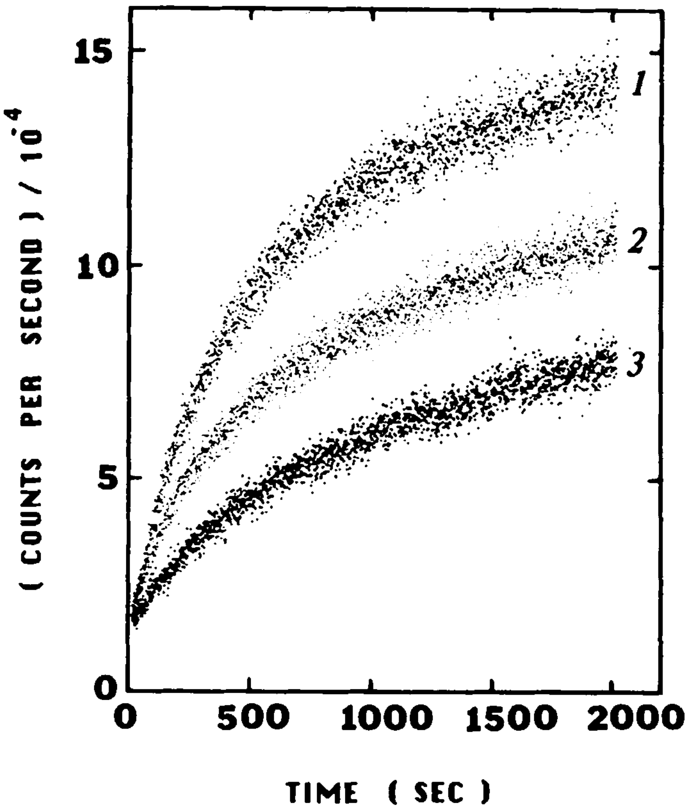

FIGURE 4 Photopolymerization kinetics in various polymer matrices: 1- Cellulose acetate butyrate, 2- Polyvinylbutyrate, 3- Vinylacetate

The behavior of the system is, naturally, more complicated than that given by the "evaporation" model described above. To understand the kinetics and mechanism of the photopolymerization we also investigated the extent to which oxygen inhibits the NVC photopolymerization. Oxygen does not quench the NVC or PVCA fluorescence which have life times on the order of several nanoseconds. Thus, our fluorescence based method of kinetic studies can be and is used by us to study oxygen effects. Oxygen forms peroxides with the radicals and growing polymer radicals, terminating the polymerization[6]. We conducted the experiment while illuminating the photopolymer film in a home-made vacuum cell equipped with sapphire windows, positioned for fluorescence observation. The cell containing the sample was evacuated and filled with the nitrogen-oxygen mixtures of varying compositions. The rate of photopolymerization is very sensitive to oxygen contents, 0.05% oxygen in nitrogen mixture changes the photopolymerization kinetics (Figure 5). These results are in a qualitative agreement with the results of the computations, which we conducted using a comprehensive kinetic scheme taking into account the diffusion of molecular species towards the illuminated surface[8].

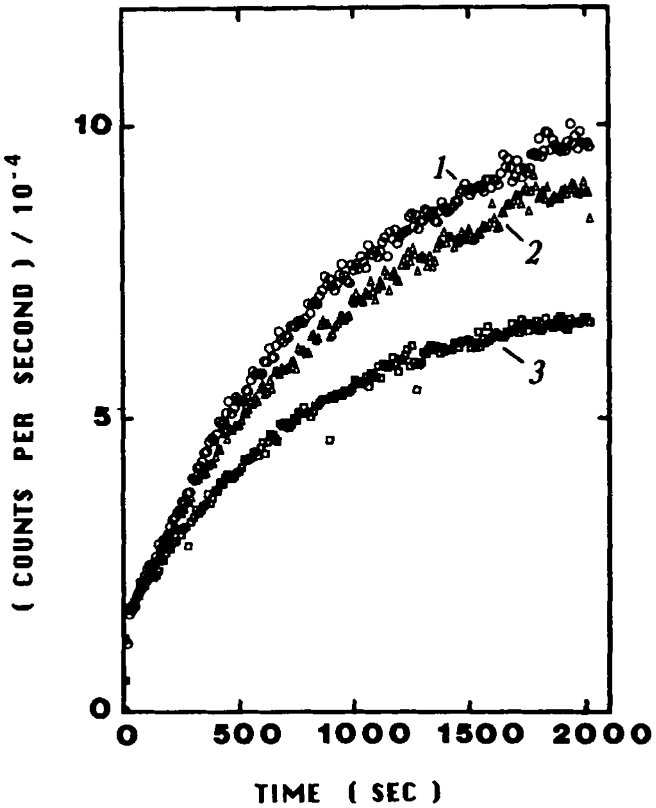

FIGURE 5 Oxygen effects on photopolymerization, measured in 1 atm of : 1- pure nitrogen, 2- 0.05% oxygen in nitrogen, 3- 5% oxygen in nitrogen.

The distribution of the photopolymerization reaction products is anisotropic. It is calculated as a function of distance from the illuminated surface and the time elapsed from the beginning of illumination using the kinetic model taking into account the unidirectional diffusion of the monomer and oxygen (Figure 6)[8]. This kinetic modeling predicted interesting behavior of the system. Since oxygen is consumed faster where the density of the radicals is the highest, namely, near the illuminated surface of the film, it also diffuses toward the light from the bulk of the film. As a result the film becomes oxygen poor some distance away from the surface and the highest amount of polymer is formed not at the surface but near it (Figure 6). This data illustrates the difficulties in uniform imaging of photopolymers encountered in some applications. At the same time these calculated results indicate the paths for the reduction of the nonuniformities.

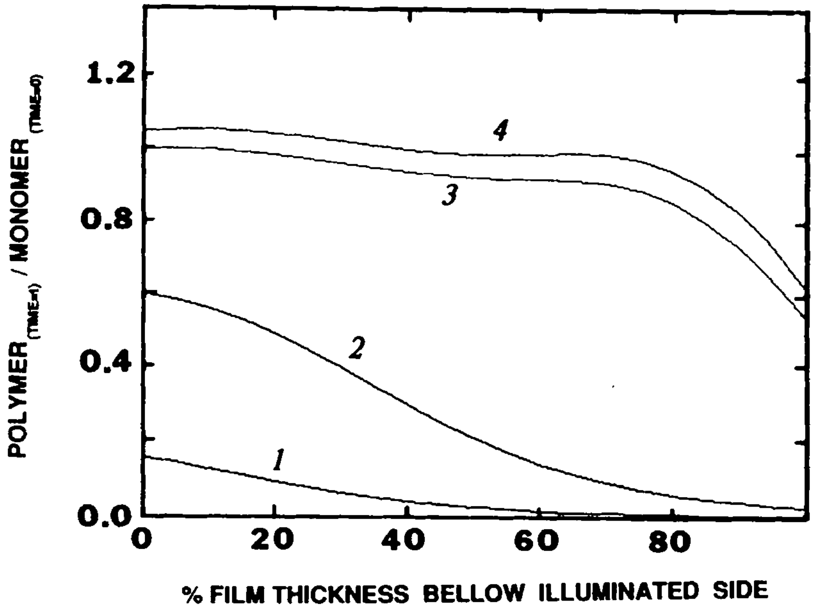

FIGURE 6 Computed concentration of formed polymer as a function of distance from illuminated surface. At times: 1- 2 seconds, 2- 10 seconds, 3- 30 seconds, 4- 40 seconds from the start of photopolymerization.

CONCLUSION

Anisotropic behavior is usually associated with liquid crystalline systems, membranes, biological systems and the reactions conducted in the presence of electric or magnetic fields. It is often forgotten that in most cases the photoinitiated reactions are inheritantly anisotropic[8-10]. In our work we utilized this anisotropy to monitor the photopolymerization kinetics and at the same time studied and modeled it.

In the course of our search for new imaging techniques and materials we developed a new, direct and nondestructive method for measuring polymerization kinetics and monomer transport in photopolymers. This method while using a straightforward experimental set-up, is useful in the investigations of a variety of photopolymers and photoresists. The extent of its versatility is well illustrated by the measurements of oxygen and matrix effects on imaging kinetics (Figures 4,5). We offer this method as a convenient tool in assisting the formulation of new imaging materials.

REFERENCES

1. A. B. Cohen and P. Walker, Imaging Processes and Materials, Neblette's 8th edition, Ed. J. M. Sturge, V. Walworth and A. Shepp, (Van Nostrand Reinhold, New York , 1989), p. 226.
2. D. E. Koppel in 'Fast Methods in Physical Biochemistry and Cell Biology', R. I. Sha'afi and S. M. Fernandez Ed., Elsevier, Amsterdam-New York-Oxford, 1983
3. B. L. Booth, Applied Optics, 14(3), 593 (1975)
4. Y. Ono, Y. Kimura, Y. Ohta and N. Nishida, Applied Optics, 26(6), 1142 (1987)
5. V. V. Krongauz and R. M. Yohannan, Polymer, in print
6. Kh. S. Bagdasar'yan, Theory of Free Radical Polymerization, (Israel Program for Scientific Translations Ltd, 1968)
7. J. Crank, The Mathematics of Diffusion, (Oxford at the Clarendon Press, 1956)
8. V. V. Krongauz, R. E. Schmelzer and R. M. Yohannan, in preparation
9. A. R. Shultz and M. G. Joshi, J. Pol. Sci., Pol. Phys. Ed., 22, 1753 (1984)
10. E. A. Lissi and A. Zanocco, J. Polym. Sci., Pol. Chem. Ed., 21, 2197 (1983)