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Photochemical Study of the Transport Properties of Gases in Polymer Films

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We describe a general method of finding the transport properties of molecules in polymer films by photolysis. Poly(methyl methacrylate) samples held at different temperatures are exposed to UV radiation at discrete wavelengths, and the time evolution of the volatile photoproducts are detected with a quadrupole mass spectrometer. A diffusion model is used to fit the experimental data and deduce diffusion coefficients for the main photoproduct methyl formate. The average value at room temperature was equal to 1.9×10^{-11} cm^2 s^{-1} at all wavelengths investigated. Together with the values derived at other temperatures, an Arrhenius plot was obtained and the activation energy for methyl formate diffusion within the polymeric thin film calculated from the slope of the graph. We envision that this new method will find application to a variety of problems involving the mass transport of molecules through boundary layers of single or multilayer thin film structures.

Introduction

The solution and transport behavior of gases in polymers is a topic of great importance because of fundamental interest and technological applications.[1,2] While polymers are usually soluble in only a very small number of organic solvents, most small molecules are soluble in polymers to some extent.[3] The importance and relevance of such behavior have become more apparent in recent years with the accelerating development of separation membrane systems, highly impermeable or selectively permeable packaging or barrier films, and the overall increase in the use of polymeric materials for diverse applications with consequent exposure to various environmental agents.[2]

To study this diffusion process quantitatively, several experimental techniques have been devised. The most common one consists of suddenly exposing one side of a film to a constant partial pressure P_1 of penetrant and measuring the partial pressure P_2 on the other side of the film.[1,3] After a time lag before any of the diffusing species reach the other side of the film, the increase in P_2 approaches a constant rate. The intercept L of this straight line on the time axis can be shown to give the diffusion constant D from the relation $L = l^2/6D$, where l is the thickness of the polymer. The drawback of this method lies in the long observation times required to measure small diffusion coefficients.[4] Other common methods include the use of a quartz crystal microbalance to measure the resonant frequency and thus mass changes of a film during diffusion,[5] gas chromatography,[3] the measurement of the diffusion controlled luminescence quenching of excited singlets in a polymer,[6] and, in the specific case of oxygen diffusion, electron spin resonance to monitor the diffusion controlled decay (via oxidation) of radicals generated by radiation (UV or γ in general).[7,8]

In this article, we describe an alternate method of studying transport properties using photolysis. This elucidation of transport properties is done by fitting a quantitative model to the transients of radiation produced gaseous species measured with a quadrupole mass spectrometer. We use poly(methyl methacrylate) (PMMA) as a model compound because of its well-known photochemistry and its numerous applications in UV photolithography and imaging.[9–11] Its photodecomposition varies according to the wavelength of the radiation. In the VUV range (10−200 nm), the high energy of the photons is sufficient to dissociatively excite any of its chemical bonds.[12,13] In the UVA range (315−400 nm), it does not undergo any degradation.[14] In between the two (200−300 nm), the presence of the ester chromophore gives it a distinct photochemistry that is different from that of most other polymers.[12]

The photolysis of PMMA results in a random scission of the polymer chain backbone by a radical process. The major reactions that have been reported to occur at the same time are shown in Figure 1.[12,15] The relative importance of each of the processes depends on the wavelength of radiation. Direct main-chain scission plays a major role at short wavelengths,[16–18] while in the classical photochemistry range ($\lambda > 200$ nm), ester side-chain scission dominates,[19–21] with methyl formate radicals •COOCH$_3$ being the major initial reaction products. The latter then quickly abstract hydrogen from the polymer backbone to form methyl formate at room temperature, which is what is detected by mass spectrometry. This mechanism has been shown by many electron spin resonance studies on the precursors of the room temperature vacuum photodegradation of PMMA where, based on the nine-line spectrum obtained, the only radical detected was the one labeled A in the reaction scheme given in Figure 1.[19–22] It originated mostly from a β-cleavage of radical
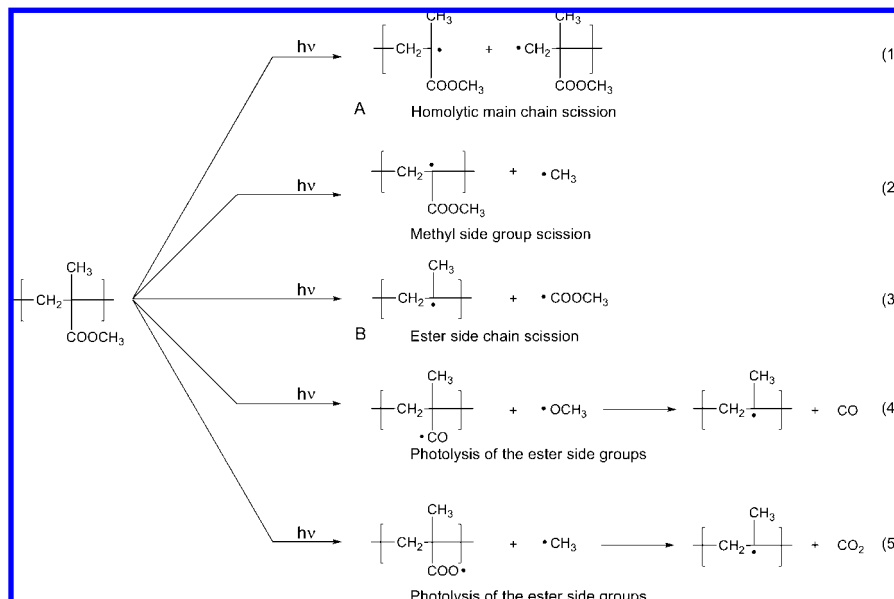
Figure 1. Initial steps in the photodegradation of PMMA.

B (Figure 1, reaction 3) but also from a homolytic main-chain scission of the polymer. The radicals $\cdot COOCH_3$ and $\cdot CH_3$ (in addition to radical A) were detected only when irradiation was carried out at liquid N_2 temperature (77 K). They were produced by ester side-chain scission as shown in reactions 3 and 4 of Figure 1 ($\cdot CH_3$ can also originate from the decomposition of $\cdot COOCH_3$). They were both found to disappear upon heating to room temperature, leaving only radical A. Furthermore, quantum yield measurements of the main photoprocesses on direct UV excitation of PMMA at room temperature by Gupta et al. have yielded a value of 0.92 for methyl formate whereas that of the methyl formate radical was only significant at 77 K where it was found to be equal to 0.70.[19] Hence, at room temperature, the lifetime of the methyl formate radical is fleeting and hydrogen abstraction occurs at a very fast rate, though to our knowledge no study has been done to determine the actual rate constant. The above-mentioned studies are in agreement with our own as volatile photoproducts were detected only at mass 60 (methyl formate), contrary to other studies where methyl formate radical was found to be the major photoproduct.[17,23]

Experimental Section

PMMA films of thicknesses 3 μm were prepared by spin-coating 20 μL of a 7.55% by weight solution of PMMA (MW 350 000 g/mol) in toluene onto Si wafers at 3000 rpm. The samples were mounted onto a manipulator inside a UHV chamber and, after pump down, baked for 10 h at 413 K to remove any residual solvent.

Photolysis was carried out using a 500 W Hg (Xe) arc lamp (Oriel model 66142) with a water filter to remove infrared radiation. A monochromator with a 1200 line/mm optical grating blazed for 280 nm and providing a bandpass ranging from 0.5 to 20 nm was used for wavelength selection. Its entrance slit was set at 0.9 mm and its exit slit at 1.0 mm. The lamp was placed outside of the chamber, at a distance of 23 cm from the sample, with the UV light irradiating the latter through a MgF_2 viewport (lower cutoff wavelength = 115 nm). The intensity of the radiation at the sample position was measured using a radiant power energy meter (Newport, Oriel Instruments 70260) and a thermopile detector (Newport, Oriel Instruments 70264).

TABLE 1: UV Light Intensity at a Selected Number of Wavelengths

λ (nm)	220	240	250	260
intensity ($\mu W/cm^2$)	43	127	150	178

The values obtained for each of the wavelengths used in this experiment are given in Table 1.

UV exposures of the sample were done at several combinations of wavelength and temperature: first at room temperature (300 K) and different wavelengths (220, 240, 250, and 260 nm) and then at constant wavelength (λ = 220 nm) and different temperatures (323, 343, and 353 K). The transients of the radiation produced gaseous species that were measured with a quadrupole mass spectrometer (UTI 100C) placed 5 cm away from the sample in such a way that the angle the latter made with both the RGA and the UV light were equal (45°). For each run, the light was turned on after taking a baseline plot of the output of the detector for 300 s and off after 3896 s of irradiation. The signal thus obtained was proportional to the instantaneous evolution rate of the volatile photoproducts. Methyl formate was the only detectable gaseous photoproduct, as expected based on the overview of the photochemistry of PMMA given earlier. The dynamics of its evolution (both when the light was on and when the light was off) were then fitted to a simple diffusion model which yielded diffusion coefficients for each combination of wavelength and temperature. From an Arrhenius plot of ln *D* vs 1/*T*, the activation energy and pre-exponential factor for the diffusion of methyl formate in PMMA were calculated.

Diffusion Model. A few assumptions had to be made in order to model the time evolution of the photoproducts. First that the film was a homogeneous layer thin enough for the light intensity to be almost uniform throughout. In the weak absorption limit (such as in the present study) where the thickness of the sample is a lot smaller than the penetration depth of the light, this assumption is valid. Table 2 lists values for the penetration depth of UV in PMMA at all the wavelengths of radiation investigated. They were derived from our own UV absorption spectra. A second assumption was that diffusion was the rate-determining step rather than the generation chemistry (i.e., the ester side-chain scission), some postirradiation chemistry (such as the hydrogen abstraction by the methyl formate radical) or surface
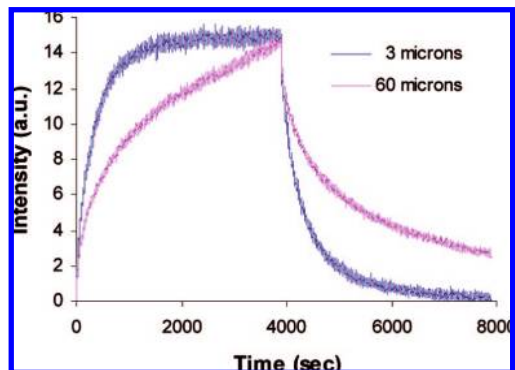
7168 *J. Phys. Chem. B, Vol. 112, No. 24, 2008*

Cisse et al.

Figure 2. Effect of sample thickness on the dynamical profile upon photoirradiation ($T = 323$ K). The difference in time-evolution profiles for these two samples, which differ only in thickness, confirms that bulk mobility and not surface desorption is the dominant contribution to the observed kinetic profiles.

TABLE 2: Penetration Depth of UV Radiation at Selected Wavelengths

λ (nm)	220	240	250	260
penetration depth (μm)	3	15	30	53

TABLE 3: Diffusion Coefficients Obtained as a Function of Temperature and Wavelength

λ (nm)	260	250	240	220	220	220	220
T (K)	300	300	300	300	323	340	353
$D \times 10^{11}$(cm^2/s)	2	2	1.5	2	15	60	150

trapping.[24] The latter possibility was ruled out after comparing the normalized dynamical profiles obtained upon UV irradiation of two samples of radically different thicknesses, Figure 2. Their drastic difference confirmed that the time evolution of the photoproducts was determined by mobility in the sample and not by desorption from the polymer surface. The diffusion was also assumed to obey Fick's second law, which is the fundamental equation of diffusion in an isotropic medium (i.e., one whose structure and diffusion properties in the neighborhood of any point are the same relative to all directions[25–27]). Finally the diffusion coefficient was assumed to be independent of concentration, time, and depth in the film and to be also unaffected by previous sample irradiation. Given these assumptions, one can write the following generalized equation for one-dimensional diffusion of the methyl formate species formed upon UV photolysis[12,25–28]

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} + \frac{\varphi a I_0 e^{-ax}}{h\nu} \tag{1}$$

where c is the concentration of methyl formate anywhere in the film, ϕ the quantum yield, a the absorption coefficient of the light, I_0 its intensity, and ν its frequency. The first term embodies the Fickian contribution, while the second one accounts for the continuous creation of methyl formate during irradiation. This second term was derived using Beer's law. When a parallel beam of light passes through a film, the intensity of the absorbed radiation per unit area at a layer of thickness dx located at a distance x from the surface can be determined to be $-dI/dx = I_0 a e^{-ax}$, where I_0 is the intensity of the light and a its absorption coefficient.[12,28]

To gain insight into the approximation method used to solve this differential equation, let us first ignore the second term in the above differential equation. The problem then becomes that of simple diffusion out of a slab for which an exact solution exists. In general, for diffusion out of both sides of a slab of
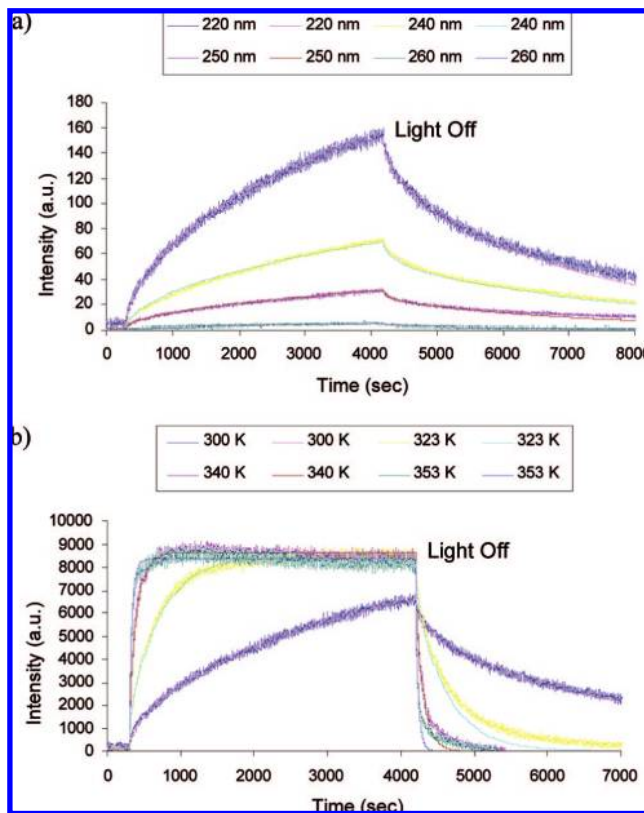

Figure 3. Presentation of the volatile product waveforms emanating from irradiated PMMA and the associated diffusion model numerical fits to the data: (a) constant T (300 K) and varying λ; (b) constant λ (220 nm) and varying T.

thickness h with a uniform initial concentration of diffusants c_0 and zero surface concentration at all $t > 0$, the solution is[25–27,29]

$$c(x,t) = \frac{4c_0}{\pi} \sum_{v=0}^{\infty} \frac{1}{2v+1} \sin\frac{(2v+1)\pi x}{h} e^{\left[-\left(\frac{(2v+1)\pi}{h}\right)^2 Dt\right]} \tag{2}$$

where D is the diffusion coefficient in units of cm^2 s^{-1}, h the thickness in centimeters, and t the time in seconds. Since $(\partial c(x,t))/\partial x = 0$ for all t at $x = 0.5$ h, the system can be cut in half by a plane at $x = 0.5$ h without affecting the concentration distribution, which is symmetrical about that plane. Therefore eq 2 is also the general solution for diffusion out of a polymer film of thickness 0.5 h on a Si wafer located at 0.5 h, with a constant initial concentration of c_0.

With some modifications to this model, one can incorporate the second driving term of the differential equation (eq 1) and fit the diffusion data. For each exposure, the output of the mass spectrometer shows a temperature-dependent rise as soon as the light is turned on followed by a temperature dependent decay as soon as it is off. Hence no induction period was ever involved. To fit the "light-on" portion of the data, one can schematically divide the continuous UV irradiation into a train of conceptual pulses lasting one second each and study their separate effect. As mentioned earlier, the PMMA samples are thin enough that the intensity of the UV light can be considered to be almost uniform throughout their bulk. Given the direct proportionality between the intensity of the absorbed radiation and the amount of methyl formate molecules created, the concentration of photoproducts in the sample upon irradiation by one such pulse would also be uniform and its time dependence monitored by

Transport Properties of Gases in Polymer Films

J. Phys. Chem. B, Vol. 112, No. 24, 2008 **7169**

TABLE 4: Diffusion Constants of Various Gases in Polymers

gas	He (ref 33)	CO_2 (ref 33)	N_2 (ref 33)	·COOD (ref 4)	CO_2 (ref 2)
D (cm²/s)	3.63×10^{-8}	4.68×10^{-9}	8.7×10^{-10}	$8 \pm 2 \times 10^{-11}$	3.7×10^{-7}
T (K)	303.2	303.2	308.2	room temperature	298.15
polymer	PMMA	PMMA	PMMA	PMMA	polyethylene

Equation 2. However, since we are actually measuring the amount of methyl formate given off, a more useful equation to which we can easily relate the output of the mass spectrometer is the average concentration given by[29]

$$C_{av}(t) = \frac{1}{h}\int_0^h c\,dx = \frac{8c_0}{\pi^2}\sum_{v=0}^{\infty}\frac{1}{(2v+1)^2}e\left[-\left(\frac{(2v+1)\pi}{h}\right)^2 Dt\right]$$

$$(3)$$

It follows then that at any time t, the contribution to the output of the quadrupole from the methyl formate species formed upon irradiation by a given ultraviolet light pulse of one second would simply be proportional to $C_{av}(t-1) - C_{av}(t)$, where t is the time since the pulse was flashed. The total output of the mass spectrometer at any time t $I(t)$ would then be proportional to the sum of t such contributions, where t is the duration of the UV exposure, which also corresponds to an equivalent number of one-second UV pulses

$$I(t) \propto \sum_{t=1}^{t} C_{av}(t-1) - C_{av}(t) = C_0 - C_{av}(t) \quad (4)$$

For the "light-off" portion of the curves, there are no new UV light pulses creating additional methyl formate species. Hence $I(t)$ would simply be proportional to the sum of the time varying contributions from methyl formate species already created by each of the previous conceptual one-second UV light pulses that irradiated the sample when the lamp was on. In this case then, one can easily see that

$$I(t) \propto C_{av}(t - t_{off}) - C_{av}(t) \quad (5)$$

where t_{off} is the time when the light was switched off.

Results and Discussion

Results of the UV irradiation of the samples at the combinations of wavelengths and temperatures mentioned earlier are shown in Figure 3. The data have been normalized to take into account the differences in light intensity at each wavelength. Fitting the data to eqs 4 and 5, we obtain the lines which overlay the data in Figure 3, where the smooth solid lines represent the numerical calculations. The diffusion constants so derived are
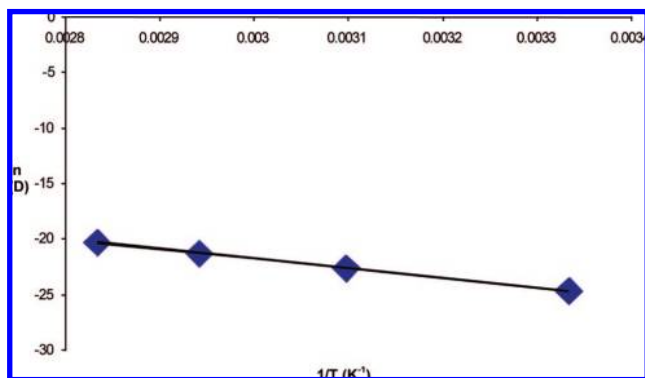

Figure 4. Arrhenius plot for the diffusion of photogenerated methyl formate in PMMA.

listed in Table 3. The fits were observed to reproduce accurately the experimental data, except for the tail end of the high temperature curves.

The room temperature diffusion coefficient was found to be essentially the same at all UV wavelengths (2×10^{-11} m/s²). We can then conclude that the wavelength of the radiation has no effect on the diffusion constants. This outcome is expected since the only difference between irradiations performed at different wavelengths lies in the absorption coefficient of the UV light, which translates into different concentrations of diffusing molecules. And since the latter was assumed (reasonably as it turned out) to have no effect on the diffusion coefficient, no wavelength variation in D should be expected.

Data on the diffusion of large molecules within PMMA are not readily available in the literature for comparison purposes. Most studies so far have focused on small common gases. Table 4 lists the diffusion constants for some of them. On the basis of these data, two factors seem to affect the diffusion coefficient. One is the medium through which diffusion occurs. For a given penetrant, the value of D decreases as the polymer chain becomes less flexible and less free volume is available.[3,30–32] This behavior explains why CO_2 has a higher diffusion coefficient in polyethylene than in PMMA at room temperature. Another factor is the size of the penetrant gas. For a given film (in this case PMMA), the value of D is inversely proportional to the size of the diffusant. This is a well-known fact from diffusion theory.[3,30–32] Diffusive motion occurs by a series of hops as free volume is opened up by segment motion in spaces adjacent to the moving molecule.[3] The larger the molecule, the larger the free volume required for diffusion to occur. Hence one would reasonably expect D to be inversely proportional to the size of the diffusant at a given temperature as more energy (i.e., a higher activation energy) will be required to create larger free volumes. This trend explains why ·COOD, which has the highest molecular weight (MW = 46) among the gases listed in Table 4, also has the lowest D ($8 \pm 2 \times 10^{-11}$ cm² s⁻¹). Methyl formate, whose molecular weight is 60, is therefore expected to have an even lower diffusion coefficient. At room temperature, this value was found to be 2×10^{-11} cm⁻² s⁻¹ on average.

For irradiations performed at different temperatures and constant wavelength, the diffusion constant was found to increase with temperature (the increase in the amount of methyl formate evolved was solely ascribed to an increase in D since the photolysis itself is not affected by temperature[12]). This is expected given that, as inferred previously, diffusion is a thermally activated process involving small scale translational motions of both the diffusant and the medium.[3] Therefore a higher temperature provides more energy for segmental mobility which in turn increases the rate of penetrant diffusion.[3] This temperature dependence can be expressed in Arrhenius form $D = D_0 e^{-E_a/RT}$, where D_0 is the permeability index or pre-exponential factor, E_a the activation energy of the diffusion process, R the universal gas constant, and T the absolute temperature. An Arrhenius plot of ln (D) vs $1/T$ is shown in Figure 4. Since it is a straight line, the activation energy was constant over the entire temperature range of our study[33] and

was found to be equal to 71.9 kJ/mol. This value is at the high end of the usual range of activation energy values for diffusion in polymeric solids (20 to 80 skJ). Indeed, for most molecules (mostly small gases), this value is usually about 40 kJ.[3] This was expected however due to the relatively larger size of the methyl formate diffusant.[3] The same reason (i.e., penetrant size) also accounts for the relatively large value of the pre-exponential factor D_0 (4.2 compared to less than 2 in general for small molecules diffusing in polymers). Indeed the latter is dependent on the entropy of activation and the jump length, and its magnitude is expected to increase with the size of the penetrant molecule.[33]

Finally, the assumption that the effect of previous sample irradiation on the diffusion coefficient was negligible was tested by making five successive hour-long exposures on the same sample at room temperature and 220 nm. The same D value was obtained in each case, which proved that our initial assumption was indeed reasonable. This is in part due to the fact that the photochemistry of PMMA does not involve cross-linking, which would have caused a gradual reduction in the value of D during UV irradiation.[3] Further proof of the negligible effect of previous irradiation on the diffusion constant comes from the fact that the latter is unchanged even if one only fits the first few data points after the light is turned on rather than the whole curve. This would not have been the case had D been changing with exposure time.

Conclusion

In conclusion, we have described a general method of finding the transport properties of molecules in polymers in the thin film limit using photolysis. Here PMMA samples were held at different temperatures and exposed to UV radiation at discrete wavelengths in concert with monitoring the time evolution of the volatile photoproducts as detected by a quadrupole mass spectrometer. A diffusion model was then used to fit the experimental data and deduce diffusion coefficients for the main photoproduct emanating from the photolyzed PMMA, methyl formate. This technique can be used optimally in the limit of low integrated photon flux, thereby limiting the effect of past irradiation on the transport properties of the polymer. It can also be generalized to the study of diffusion in even thicker polymer films provided one uses ultraviolet radiation with low absorption coefficient, (and hence high penetration depth) as this would ensure the uniformity of the light intensity throughout the sample. Finally, it may not be limited simply to the study of the diffusion of gaseous species that are produced by photolysis of their parent polymer molecule. Indeed, it should be also applicable to the investigation of the transport properties of photodissociable or other photoreleased molecules embedded in a polymer film. Alternatively, one could spin-coat a layer of such diffusants underneath the film through which they can then diffuse upon photolysis. Both techniques would obviously work provided the polymer itself were essentially transparent to the radiation.

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