

Real-Time Monitoring of Diffusion in Polymer Films Using Fluorescent Tracer

V. V. KRONGAUZ,^{1,*} W. F. MOONEY III,² J. W. PALMER,² and J. J. PATRICIA²

¹E. I. DuPont de Nemours & Company, Inc., Imaging Research and Development, P.O. Box 80352, Wilmington, Delaware 19880-0352, ²E. I. DuPont de Nemours & Company, Inc., Imaging Systems Department, New James Street, P.O. Box 505, Towanda, Pennsylvania 18848-0505

SYNOPSIS

A method for real-time nondestructive monitoring of small molecules diffusion in polymeric films was developed. The method was based on detection of a fluorescent tracer eluting from the investigated polymer film into the solution in which this film was immersed. The kinetics of the tracer elution, monitored by the increase in solution fluorescence intensity, was used to deduce tracer diffusivity in polymer film. The data were treated using a straightforward mathematical model, describing diffusion from an infinite plane of a certain thickness immersed into a finite solvent bath. Fluorescent 7-diethylamino-4-methyl coumarin was used as a tracer. The diffusion of this tracer within plasticized poly(methyl methacrylate) and styrene-isoprene-styrene block copolymer matrices was monitored. The diffusion coefficients equal to 2×10^{-9} cm²/s and 1×10^{-9} cm²/s, respectively, were obtained.

© 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric coatings and films are widely used for their resistance to permeation by environmental pollutants, water, oxygen, and corrosive agents.¹ The barrier properties of the films are, of course, related to the rate of molecular diffusion. The aging of polymer products also depends on the processes stipulated by the diffusion of small molecules in polymers (such as the loss of plasticizers). Diffusion of small molecules is a controlling factor in the performance of photoactive polymers used in imaging materials and some electronic devices.^{2,3} Interest in manufacturing of the products with characterized and predictable properties lead to recent advances in diffusion monitoring²⁻¹² and to the development of nondestructive, real-time, methods of monitoring small molecule diffusion in polymers²⁻⁴ and across polymer interfaces.¹²

Almost any change in the system associated with molecular migration can be used as a tool for the evaluation of diffusion kinetics.²⁻¹² The fluorescence intensity change is no exception, and also can be used in diffusion investigations.^{2-4,11} However, only at low concentrations of the fluorescent molecules the intensity of fluorescence is proportional to their concentration. The nonlinear dependence of fluorescence on the tracer concentration restricted the use of fluorescent methods. Previously, we described some systems and methods where fluorescence was utilized for monitoring diffusion in polymers,²⁻⁴ yet these methods required a substantial experimental sophistication. The attempts to develop more straightforward fluorescence-based methods that can be employed in an average industrial laboratory continued. A diffusion-monitoring method using fluorescent tracers was described recently by Weiss and co-workers.¹¹ They monitored, in a transmission mode, fluorescence emitted by the tracer remaining in polymer immersed in solvent, into which the tracer was eluting out of the polymer. The fluorescence emission of the tracer, which has diffused out of the polymer into the solvent, was quenched by an appropriate quencher.¹¹ We tested this technique and found it acceptable for monitoring diffusion in

* To whom correspondence should be addressed at DSM Desotech Inc., Fiber Optic Materials Department, 1122 St. Charles St., Elgin, IL 60120.

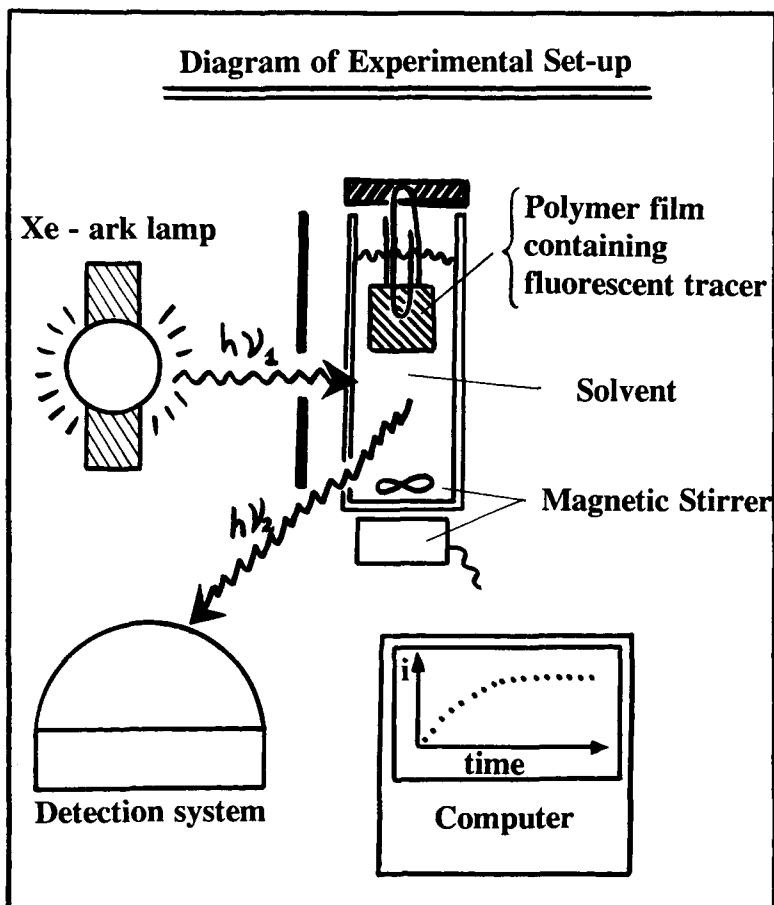


Figure 1 Diagram of the experimental setup.

transparent thin films of some of the polymers employed in photoimaging. However, this method of diffusion monitoring required deoxygenation of the system and selection of a specific fluorescent tracer and quencher combination. Monitoring fluorescence emission from the polymer itself imposed a severe restriction on the type of polymers to which the method of ref. 11 could be applied. Thus, it was prohibitively difficult to monitor fluorescence emission from the pigmented or composite polymers in a suggested¹¹ transmission mode. Additional problems encountered in finding the proper fluorophore-quencher combination prompted us to develop an alternative approach to diffusion monitoring. The straightforward technique for the real-time monitoring of molecular diffusion in polymer films using a fluorescent tracer is described below. The method described below can be used with pigmented and nontransparent materials frequently employed in barrier, imaging, and decorative coatings.

EXPERIMENTAL

Principle of the Method

It can be generalized that the rate of molecular diffusion in low viscosity solvents is substantially higher than in a polymer matrix. When the polymer film containing tracer molecules is immersed into liquid, which is not absorbed by the polymer and in which the tracer is highly soluble, the rate of the tracer migration from the polymer to a solvent is controlled by the diffusion of tracer within the polymer.^{11,12} When the tracer is fluorescent, its accumulation in solution can be monitored by an increase in intensity of fluorescence emitted by the solution. At low concentration of the tracer in solution the fluorescence intensity is proportional to the concentration of the tracer, which diffused out of the polymer.^{2,3} The kinetics of solution fluorescence intensity increase is controlled by the rate of tracer diffusion within the polymer, and can be used to deduce the diffusion coefficient of tracer in the polymer.

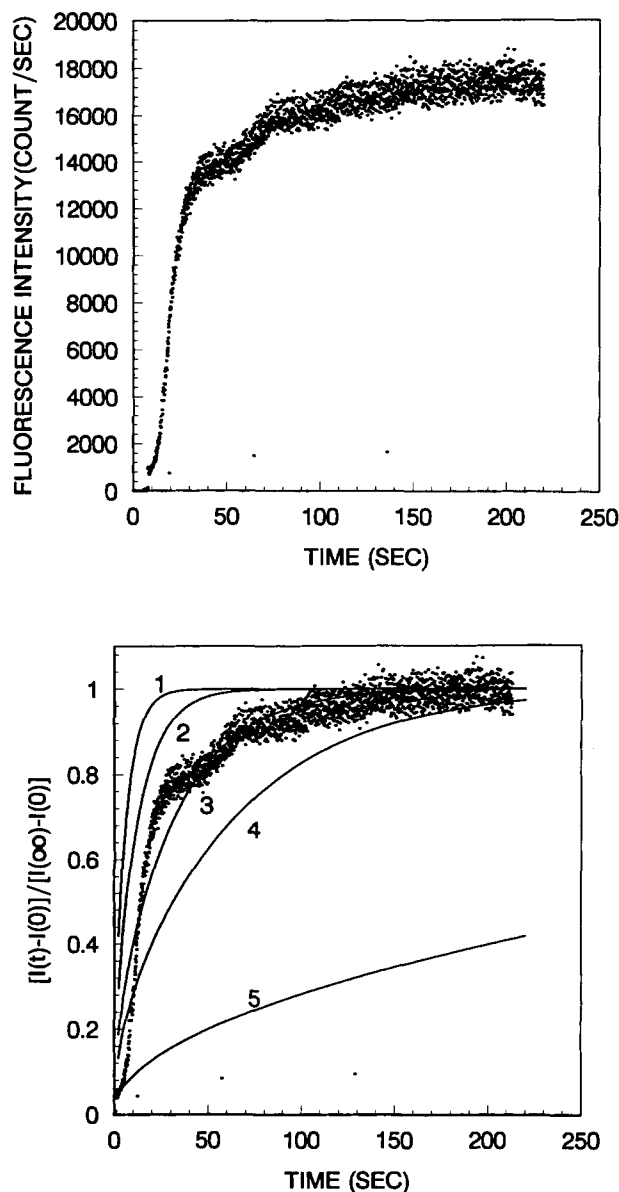


Figure 2 (a) Dependence of solution fluorescence intensity on time elapsed from the immersion of $4\ \mu\text{m}$ thick, poly(methyl methacrylate) film containing fluorescent tracer into the solvent (methanol). (b) Dependence of normalized fluorescence intensity on time elapsed from the immersion of the tracer doped, $4\ \mu\text{m}$ thick poly(methyl methacrylate) film into the solvent. Solid lines represent data computed using tracer diffusion coefficients in film as a parameter. The values used in computations were: (1) $1 \times 10^{-8}\ \text{cm}^2/\text{s}$; (2) $5 \times 10^{-9}\ \text{cm}^2/\text{s}$; (3) $2 \times 10^{-9}\ \text{cm}^2/\text{s}$; (4) $1 \times 10^{-9}\ \text{cm}^2/\text{s}$; and (5) $1 \times 10^{-10}\ \text{cm}^2/\text{s}$.

For simplicity of experimentation, a tracer should fluoresce in a chosen solvent even at ambient atmosphere and temperature, so that increase in its concentration in solution can be easily detected. Use

of the tracers fluorescing under the ambient conditions makes our technique easier to implement than that proposed by Weiss and co-workers.¹¹ Mathematical modeling is applied to deduce tracer diffusion coefficient from the kinetics of fluorescence intensity increase. To make numerical modeling and data deconvolution straightforward, the selected solvent should not dissolve or swell the studied polymer film. More detailed modeling, taking into account the difference in diffusion coefficients in the polymer film and in the solution, was constructed by us previously,¹² and can be used when higher precision is required.

To monitor the fluorescence of the tracer eluting from the polymer to solvent, the polymer film should be placed above the optical path of the excitation light. Thus, only the fluorescence emitted by the dissolved tracer will be detected. An entire film sample should be immersed to ensure material balance in the system (Fig. 1). The solution is stirred to reduce possible concentration gradients.

Materials and Reagents

Due to particular manufacturing requirements, the diffusion in two specific polymer films was studied. One film consisted of 39% of poly(methyl methacrylate) (ElvaciteTM 2051, $M_w = 350,000$, $T_g = 105^\circ\text{C}$, DuPont Co.) and 53% of high molecular weight reactive diluent (an unsaturated polyester resin, HetronTM Q6332, consists of nonfluorescent species with $M_w = 481$ (80%), and $M_w > 5,000$ (20%), Asland Chemical Co.). This polymer film was UV cured after coating before the measurements. Another film was made using 100% styrene-isoprene-styrene block copolymer (KratonTM D1107, $M_w = 10,000 \div 50,000$, $T_g \approx -65^\circ\text{C}$, Shell Chemical Co.).

The polymer films were coated from dichloromethylene (spectroscopically pure, Aldrich Co.) solution on a polyethylene terephthalate sheet (MylarTM, DuPont Co.) for ease of handling. Coatings of poly(methyl methacrylate) were $4\ \mu\text{m}$ thick, whereas those of styrene-isoprene-styrene block copolymers were $9\ \mu\text{m}$ thick. The coating of the sample film on the support is not a prerequisite for the described technique. Free-standing doped films can be used as well.

The method was developed to measure diffusion in only minimally modified commercially available coatings. In proofing coatings, 3% of 7-diethylamino-4-methyl coumarin was usually added as a fluorescent brightener. To maintain the experiments close to the real systems, 3% of 7-diethylamino-4-methyl coumarin (BASF Corp.) was used as a fluorescent

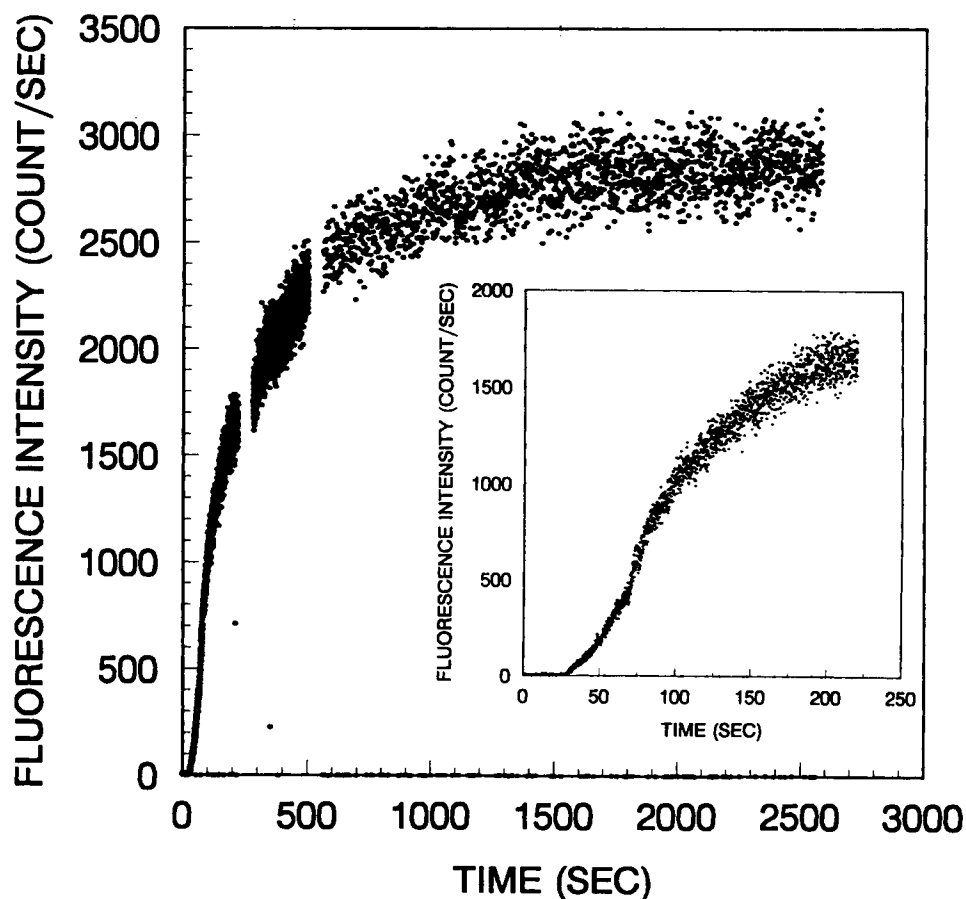


Figure 3 (a) Dependence of fluorescence intensity of solution on time elapsed from the immersion of the $9\ \mu\text{m}$ thick, styrene-isoprene-styrene block copolymer film containing fluorescent tracer into the solvent (methanol). The data for short times is shown in the insert. (b) Dependence of normalized fluorescence intensity of solution on time elapsed from the immersion of tracer doped, $9\ \mu\text{m}$ thick styrene-isoprene-styrene block copolymer film into solvent. The data for short times is shown in the insert. Kinetic curve computed using diffusion coefficient $D = 1 \times 10^{-9}\ \text{cm}^2/\text{s}$ (solid line) correlated well with the experimental data.

tracer. However, the method had very high sensitivity and the tracer levels $\ll 1\%$ gave excellent fluorescence emission signal-to-noise ratio.

Methanol (spectroscopically pure grade, Aldrich Co.) was selected as a solvent because it did not dissolve any other ingredients of the film besides the fluorescent tracer. Penetration and swelling of the films used in the experiments by methanol was determined to be insignificant ($\ll 1\%$ by wt.). All components and support film were checked to ensure the absence of fluorescence of other molecules besides 7-diethylamino-4-methyl coumarin, selected as a tracer. It was verified that there were no reactive or quenching impurities in the solvent into which the polymer film containing the tracer was immersed. The support films also did not have any

reactants or quenchers that could leach out into the alcohol solution.

Instrumentation and Run Procedure

The experiments were conducted in a $1.0 \times 1.0\ \text{cm}$ quartz cell equipped with a magnetic stirrer at the bottom (cell 109.00 of Cuv-O-StirTM system, Model 333, Hellma GmbH & Co., D-7840 Mullheim/Baden). Stirring rate did not affect the observed kinetics of fluorescence intensity increase. The cell was illuminated by a 150 W xenon-arc lamp (Oriel Corp.). The source light was filtered through a water filter, conventional interference filter, and, after passing through a monochromator (Bausch and Lomb Co.), was focused on a cell. Emission was

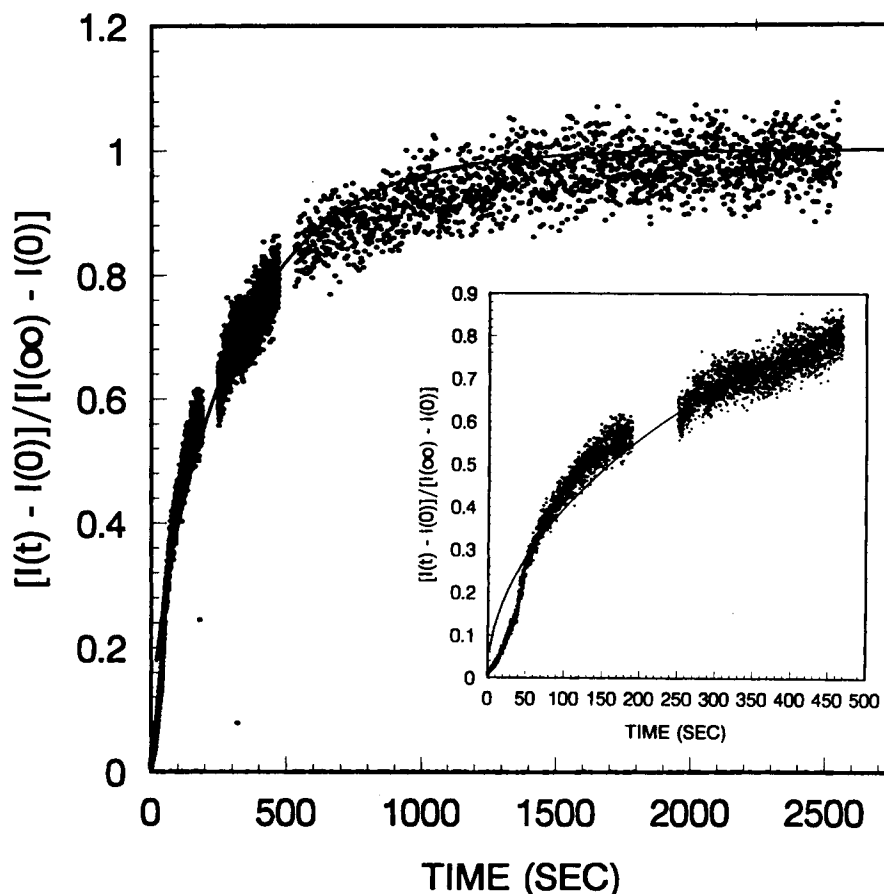


Figure 3 (Continued from previous page)

monitored at a 90° angle relative to the incidence direction of the excitation light. Fluorescence was excited at the wavelength of 360 nm, and the emitted fluorescence was detected at 450 nm. After passing through a conventional bandpass filter and monochromator (Bausch & Lomb Co.), the emitted light was monitored using a 2" head-on photomultiplier tube (R-329-02, Hamamatsu Photonics K.K.). The signal was amplified by a 300 MHz preamplifier (SR-440, Stanford Research Systems Inc.) and digitized by a gated photon counter (SR-400, Stanford Research Systems Inc.). The signal was then recorded using a personal computer (Hewlett Packard HP Vectra). A detailed description of the experimental setup can be found elsewhere.^{2,3}

In a typical experimental run, the sample cell equipped with magnetic stirrer was filled with methyl alcohol and placed under the excitation light into the system described above. After the signal monitoring began, the film sample, equipped with a stopper to prevent it from crossing the optical path of the excitation light, was quickly lowered into the solvent (Fig. 1). The fluorescence emission was re-

corded as a function of time until there was no observable change in its intensity [Fig. 2(a)]. The recorded signal [Fig. 2(a)] was further processed or used to determine the time required to complete partitioning of the tracer between the film and solution.

RESULTS AND COMPUTATIONS

Model and Computations

The experimental data lends itself to a straightforward interpretation and computer modeling. Due to the gradient between concentration of the tracer in the polymer film and in the solvent, tracer elutes out of the film into the solvent until an equilibrium concentration is reached. The exact mechanism of the tracer diffusion inside the polymer film was not studied. The process was treated following a generally accepted approach^{2-4,11-14} considering the diffusion as a process analogous to heat transfer. In such an approach, influences of the molecular struc-

ture and interactions are assumed implicitly accounted for within the apparent diffusion coefficient. This apparent diffusion coefficient can be further analyzed as a function of diffusing molecules cross-sections, media porosity, and media-tracer interactions using molecular dynamics methods.¹⁵ In the present work, a standard phenomenological description of diffusion was employed.^{13,14}

The solution was well stirred so that the concentration of the tracer throughout the solvent was considered equal. Changing the rate of stirring did not alter the tracer elution kinetics. No tracer was initially in the solution, so the observed process was regarded as equivalent to dissolution from a plane sheet into a finite solvent bath or evaporation into a finite volume. Thickness of the film (4 or 9 μm) was several orders of magnitude lower than its width (1 cm) and length (1 cm). Thus, the amount of material diffusing through the boundary was relatively small, and the boundary problem was neglected in a first approximation. The permeability of the MylarTM support to the tracer molecules was insignificant relative to that of the polymer films containing the tracer and was neglected. The independent experiments were performed to verify that tracer diffusion through MylarTM support did not occur over the time of the measurements. The problem of diffusion-controlled tracer dissolution from one side of a plane sheet was solved analytically for the time dependence of the tracer amount leaving the film.^{13,14} The solution cited by Crank^{13,14} was further simplified.² Although finite, the volume of the solution in the 1×1 cm optical cell was substantially larger than that of 1 cm² piece of 4 μm or 9 μm thick film. When the volume of the solvent is much larger than that of the film, the following equation can be used to describe the rate of tracer elution:²

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

where $M(t)$, $M(0)$, and $M(\infty)$ represent the mass of eluted tracer in solution at times t , beginning of the measurements, and at the end of the experiment, respectively. The β_n coefficients were tabulated for up to $n = 6$, and explained in detail elsewhere.^{13,14} D (cm²/s) is the diffusion coefficient of the tracer molecule in polymer film, and x (cm) is the polymer film thickness. The diffusion kinetics described by the above equation were computed using the diffusion coefficient of the tracer molecule in film as a

parameter [Fig. 2(b)]. Let $I(t)$, $I(0)$, and $I(\infty)$ represent fluorescence intensities of the solution at times t , at the beginning and at the end of the experiment, respectively. At low concentrations of fluorophore used here the fluorescence intensity was proportional to fluorophore concentration. Thus, the normalized change in fluorescence intensity $[I(t) - I(0)]/[I(\infty) - I(0)]$ was equal to the normalized mass of tracer leaving the film and accumulating in the solution, $[M(t) - M(0)]/[M(\infty) - M(0)]$. The experimentally determined values of $[I(t) - I(0)]/[I(\infty) - I(0)]$ were compared with those computed using the tracer diffusion coefficient as an adjustable parameter. The diffusion coefficient describing the system was obtained by superimposing the experimental and computed results [Fig. 2(b)].

Tracer Diffusivity in Polymer Film

Within the constraints of the selected diffusion model, the best fit for 7-diethylamino-4-methylcoumarin diffusion in plasticized poly(methyl methacrylate) (ElviciteTM 2051) was obtained with the diffusion coefficient $D = 2 \times 10^{-9}$ cm²/s. The multiple-computed curves are presented to illustrate the sensitivity of the method [Fig. 2(a,b)]. Similarly, tracer diffusion was monitored for a 9 μm thick film of styrene-isoprene-styrene block copolymer (KratonTM D1107). The diffusion of the tracer in this polymer was slower than in poly(methyl methacrylate), judging by the tracer elution kinetics [Fig. 3(a)]. Tracer diffusion within poly(methyl methacrylate) was well described by the selected model using the tracer diffusion coefficient, $D = 1 \times 10^{-9}$ cm²/s [Fig. 3(b)].

DISCUSSION

The goal of the described work was to develop a technique for real-time monitoring of diffusion in polymers requiring minimum effort and using only easily available instrumentation. Most of the experiments described here can be conducted with the majority of the polymers using a conventional spectrofluorimeter, and recording fluorescence intensity several seconds or even minutes apart. The choice of the fluorescent tracer is, naturally, stipulated by the size of the diffusing molecules one wishes to imitate, and also depends on the desired spectroscopic characteristics of the tracer molecule.

We have chosen a relatively long excitation wavelength to prevent the photolysis of 7-diethylamino-4-methylcoumarin. Other tracers can be em-

ployed under different conditions. The solvents can also be varied, depending on the polymer and the tracer used. Although the described technique has its limitations, it is an attractive and straightforward tool for real-time, nondestructive monitoring of small molecules diffusion in a wide variety of polymeric systems. The factor limiting the range of applications, as in most other methods, is the time required to position the film sample. In the present case, less than 2 s were needed to drop the film (set in the holder) into the solution. This time was much shorter than that of the entire measurement interval and did not significantly alter the results. To eliminate the error introduced by the start-up time, the thicker films can be used in the measurements. The method applications can be also restricted to slower processes. The effects of the film thickness on diffusion-controlled kinetics of tracer elution from the film to the solvent are illustrated by the data presented above for styrene-isoprene-styrene films [Fig. 3(a) vs. Fig. 2(a)].

The developed technique did not require special consideration of light absorption by the polymer, as was the requirement for the application of other techniques.¹¹ The quenching properties of the polymer film also did not interfere with our measurements. Only the requirement that the small molecules used as fluorescent tracers "must be somewhat soluble in a solvent which both, does not absorb the excitation or emission light, and exhibits very low permeability into the host polymer"¹¹ must be satisfied. A more sophisticated model of the process can take into account swelling of the film during the measurements, eliminating some difficulties connected with the choice of solvent and expand method applications.

The mathematical model used to derive the diffusion coefficients from the experimental data can be further modified to take into account the loading time and exact differences in film and solution volumes. Other factors influencing the tracer diffusion such as differences of tracer diffusivity in polymer film and in solvent can be included as well.¹² Variable

diffusion coefficient also can be introduced. However, the advantage of the presented method is in the simplicity of concept, interpretation, and application. The described method is particularly suited for comparing diffusion rates in various polymer films.

REFERENCES

1. F. W. Billmeyer, Jr., *Textbook of Polymer Science*, John Wiley & Sons, New York, 1984.
2. V. V. Krongauz and R. M. Yohannan, *Polymer*, **31**(6), 1130 (1990).
3. V. V. Krongauz, E. R. Schmelzer, and R. M. Yohannan, *Polymer*, **32**(9), 1654 (1991).
4. V. V. Krongauz and D. Reddy, *Polym. Commun.*, **32**(1), 7 (1991).
5. J. E. Guillet, in *Photophysical and Photochemical Tools in Polymer Science*, M. A. Winnik, Ed., D. Ridet Publishing Co., Dordrecht, Boston, Lancaster, Tokyo, 1986.
6. D. Y. Chu, J. K. Thomas, and J. Kuczynski, *Macromolecules*, **21**, 2094 (1988).
7. G. G. Belford, R. L. Belford, and G. Weber, *Proc. Natl. Acad. Sci. USA*, **69**(6), 1392 (1972).
8. T. Y. Shiah and H. Morawetz, *Macromolecules*, **17**, 792 (1984).
9. K. J. Shea, G. J. Stoddard, and D. Y. Sasaki, *Polym. Prepr.*, **27**(2), 344 (1984).
10. B. A. Smith, *Macromolecules*, **15**, 469 (1982).
11. a) Z. He, G. S. Hammond, and R. G. Weiss, *Macromolecules*, **25**(1), 501 (1992); b) L. Lu and R. G. Weiss, *Macromolecules*, **27**(1), 219 (1994).
12. V. V. Krongauz, W. F. Mooney, III, and E. R. Schmelzer, *Polymer*, **35**(5), 929 (1994).
13. J. Crank, *The Mathematics of Diffusion*, Clarendon Press, Oxford, 1956.
14. J. Crank and G. S. Park, Eds., *Diffusion in Polymers*, Academic Press, London, 1968.
15. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley & Sons: New York, 1964.

Received September 6, 1994

Accepted December 5, 1994