the melting of gels with the experiments on the destruction of the network particles after they have been cooled to form a gel.

Nevertheless, it is interesting to compare the results in Figure 6 and 7. In Figure 6 we plotted the time required to destroy the memory of stirring (i.e., to destroy most of the network particles formed by stirring) as a function of temperature, and in Figure 7 the time required to dissolve wet gels as a function of temperature. These two curves are surprisingly similar and suggest that the structure of the gel at these high temperatures may have reverted to that of the network particles. The DSC results in Figure 8 show two sharp peaks and one broad peak at a higher temperature. The two sharp peaks are probably due to the melting of platelet crystals (double peaks are often seen due to annealing during heating[25] and the broad peak is very similar to that seen in dry shish kebabs and is associated with the melting of the cores). However, as far as we know, there is no previous work on the melting behavior of shish kebabs surrounded by their mother liquor. The similarity of the memory effects of the gels of Figure 6 and 7 and the DSC results of Figure 8 allow us to speculate on the nature of the network junction zones as they are formed during shearing. The results quoted above strongly suggest that these junctions have a crystalline nature. Accordingly, we postulate that these may be localized regions of the flow field where the shear rate is sufficiently high to extend portions of the molecules. Such extended chain portions may then form crystals on coalescence with other locally extended chain portions nearby.

To summarize: We believe the work presented here shows that when solutions of high molecular weight polyethylene are stirred, network particles which can lead to gels on subsequent cooling are formed even at temperatures as high as 140 °C and concentrations as low as 0.2% (w/w). These particles once formed, although of a temporary nature, are nevertheless remarkably stable. They persist for as long as 5 h at 120 °C and as long as 0.75 h at 150 °C as can be seen in Figure 6. A gel once formed and reheated is even more stable as evidenced by Figure 7. Similar results have been reported for other polymers, and these may have the same underlying causes. If this were so, our work on polyethylene would correspond to a special case within a phenomenon of more overriding validity. This possibly special case has the advantage that we know that polyethylene does crystallize and we are familar with the temperatures of formation and melting of its various crystals morphologies. In any event, within its more confined limits, the relevance of the present results to crystallization, gelation, and fiber formation of polyethylene, the subject of our initial interest, remains upheld.

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References and Notes

(1) Barham, P. J.; Hill, M. J., Keller, A. *Colloid Polym. Sci.* **1980**, *258*, 899.
(2) Zwijnenburg, A.; Pennings, A. J. *Colloid Polym. Sci.* **1976**, *259*, 868.
(3) Smith, P.; Lemstra, P. J.; Kalb, B.; Pennings, A. J. *Polym. Bull.* **1979**, *1*, 33.
(4) Kalb, B.; Pennings, A. J. *Polymer* **1980**, *21*, 3.
(5) Smith, P.; Lemstra, P. J. *J. Mater. Sci.* **1980**, *15*, 505.
(6) Keller, A.; Barham, P. J. *Plast. Rubber Int.* **1981**, *6*, 19.
(7) Pennings, A. J. *J. Polym. Sci., Polym. Symp.* **1977**, *No. 59*, 55.
(8) Lodge, A. S. *Polymer* **1961**, *2*, 195.
(9) Peterlin, A.; Turner, D. T. *Nature (London)* **1963**, *197*, 488.
(10) Burrow, S. Peterlin, A.; Turner, D. T. *J. Polym. Sci., Polym. Lett. Ed.* **1964**, *2*, 67.
(11) Peterlin, A.; Turner, D. T. *J. Polym. Sci., Polym. Lett. Ed.* **1965**, *3*, 517.
(12) Peterlin, A.; Quan, C.; Turner, D. T. *J. Polym. Sci., Polym. Lett. Ed.* **1965**, *3*, 521.
(13) Matsuo, T.; Pavan, A.; Peterlin, A.; Turner, D. T. *J. Colloid Interface Sci.* **1967**, *24*, 241.
(14) Yamamoto, M. *J. Phys. Soc. Jpn.* **1956**, *11*, 413.
(15) Yamamoto, M. *J. Phys. Soc. Jpn.* **1957**, *12*, 1148.
(16) Yamamoto, M. *J. Phys. Soc. Jpn.* **1958**, *13*, 1200.
(17) Phan-Thien, N.; Tanner, R. I. *J. Non-Newtonian Fluid Mech.* **1977**, *2*, 353.
(18) Fuller, G. G.; Leal, L. G. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 531.
(19) Acierno, D.; La Mantia, F. P.; Marrucci, G.; Rizzo, G.; Titomanlio, G. *J. Non-Newtonian Fluid Mech.* **1976**, *1*, 125.
(20) Doi, R.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 38.
(21) Huppler, D.; Macdonald, I. F.; Ashare, E.; Spriggs, T. W.; Bird, R. B.; Holmes, L. A. *Trans. Soc. Rheol.* **1967**, *11*, 181.
(22) Osaki, K.; Ohta, S.; Fukuda, M.; Kurata, M. *J. Polym. Sci.* **1976**, *14*, 1701.
(23) Osaki, K.; Bessho, N.; Kojimoto, T.; Kurata, M. *J. Rheol.* **1979**, *23*, 457.
(24) Lockyer, M. A.; Walters, K. *Rheol. Acta* **1976**, *15*, 179.
(25) Harrison, I. R. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 991.
(26) The terms "stronger" and "weaker" are used to express the coherence of the gels, i.e., the tendency of the gels to remain in one coherent piece under comparable conditions of handling Quantitative assessment of these properties is in progress.

Measurement of Diffusion in Polymer Films by Fluorescence Redistribution after Pattern Photobleaching

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ABSTRACT: Fluorescence redistribution after pattern photobleaching has been used to measure the translational diffusion of a small probe molecule in a glassy polymer film. A new method has been developed employing a pattern mask with submicron dimensions to allow very slow diffusion ($D \approx 10^{-13}$ cm^2/s) to be measured on a convenient time scale. The diffusion coefficient of a fluorescent dye, 7-(diethylamino)-4-nitrobenz-2-oxa-1,3-diazole, in a 1-μm-thick film of poly(methyl methacrylate) containing approximately 18% residual solvent (chlorobenzene) was found to be $D = 1.6 \times 10^{-13}$ cm^2/s at 25 °C.

Introduction

Recent progress in theories to describe the dynamics of polymer melts and concentrated solutions[1,2] challenges the experimentalist to make measurements of molecular dynamics in these regimes. A few experiments have already provided validation for scaling laws within certain limits.[3-5] There are many questions yet to be answered about molecular dynamics in these systems,[6] and new measurements are needed to help answer these questions. This paper describes a method for measuring translational diffusion which is suitable for application to polymer systems over a wide range of diffusion rates. This method can make a valuable contribution to the knowledge of molecular motions in concentrated systems.

Polymer films are widely used in the electronics industry as lithographic materials. The lithographic process is based upon the property of the polymer that exposure to some form of radiation causes a change in the rate of dissolution of the film in a solvent. Penetration of solvent into the polymer film, the first step in the dissolution process, is governed by the diffusion coefficient of the solvent in the polymer matrix, which is a function of solvent concentration, and also by the rate at which the polymer matrix can swell. Thus the solvent diffusion coefficient has a strong effect on the dissolution rate of polymer films.[7,8]

In order to understand the effects of film composition, method of preparation, and exposure to radiation on dissolution rate, it is necessary to know the diffusion coefficient of solvent molecules in a polymer film. Measurements of diffusion in bulk polymer samples may not be applicable to this question, since the thin (on the order of 1 μm) dimension of these films and their method of preparation give them a unique structure. Since the diffusion coefficient depends strongly on solvent concentration, methods which rely on the observation of the decay of a substantial concentration gradient can be difficult to interpret. In addition, when slow diffusion is to be measured, it is difficult to establish concentration gradients on the small size scale which allows the measurement to be completed in a convenient time.

This paper describes a method by which the diffusion of a small fluorescent molecule (a solvent analogue) in a polymer–solvent system can be observed over any distances accessible to optical systems using visible light. Since the fluorescent dye can be detected in very low concentration, its presence does not perturb the structure of the polymer matrix. In this low-concentration limit, it can safely be assumed that the diffusion coefficient of the dye is not a function of its concentration. Since the polymer molecules in the glassy state are virtually immobile on this time scale, the measured value is a dye–solvent mutual diffusion coefficient within the polymer matrix.

Fluorescence redistribution after pattern photobleaching (FRAPP)[9] has been successfully employed to measure diffusion in several synthetic[10,11] and biological membranes.[12,13] There are several aspects of this technique which make it suitable for measurements on thin polymer films. The sensitivity of fluorescence detection allows a very low concentration of dye to be used, even in a 1-μm film. Diffusion can be followed over a distance of 0.5 μm, which in the present case allows the measurement to be completed in less than 1 h. (The measurement would require one million times longer for diffusion over a 0.5-mm distance.) This method suffers from the obvious disadvantage that only the diffusion of fluorescent molecules can be measured. This should not be a very serious problem, however, since for small molecules in a polymer matrix, the diffusion coefficient is not very sensitive to the detailed structure of the small molecule but depends primarily on its size and general shape.[14]

Principles

Fluorescence redistribution after pattern photobleaching makes use of certain fluorescent dyes which can be irreversibly photochemically bleached by intense light. Initially, the fluorescent dye is uniform in concentration throughout the sample. An intense burst of light, usually from a laser, is used to destroy the dye molecules in selected regions of the sample. Diffusion of the remaining dye molecules into the bleached regions is monitored to measure the diffusion coefficient. The sample is bleached with a striped pattern to yield alternating bands of high and low dye concentration. The periodic dependence of concentration on position leads to a simple solution to the diffusion equation and easy interpretation of the data.

There are several methods for forming a periodic pattern of light intensity on the sample, including the projection of an image[9] and the use of the interference pattern formed by the intersection of two coherent beams of light. In the present example, the pattern is formed by a metal shadow mask which is in direct contact with the polymer film. The mask has opaque lines separated by equally wide transparent spaces, to produce a square wave pattern of light intensity on the sample. This contact mask is used to avoid motion of the pattern with respect to the sample during the measurement.

After the initial high-intensity burst of light to bleach the molecules in the illuminated regions, the sample is illuminated through the mask by a low-intensity observation beam. The diffusion of fluorescent molecules into the bleached regions is observed by measuring the fluorescence intensity from these regions, which under these conditions is directly proportional to the dye concentration. Of course, this technique selectively measures diffusion in the particular direction of the initial concentration gradients. In this case, that direction is parallel to the plane of the film.

Theory

This mathematical analysis of an idealized situation will be followed by a discussion of the experimental realities. Since the diffusion coefficient of the dye is independent of its concentration, and gradients in the concentration are created by the striped pattern in only one direction, we can use the simple one-dimensional diffusion equation

$$\frac{\partial C(x,t)}{\partial t} = D\frac{\partial^2 C(x,t)}{\partial x^2} \tag{1}$$

in which C is the concentration of the dye molecule, x is the spatial coordinate, t is time, and D is the diffusion coefficient. The initial conditions established by the photobleaching are

$$C(x,0) = A + \sin(ax) + \tfrac{1}{3}\sin(3ax) + \tfrac{1}{5}\sin(5ax) + \ldots \tag{2}$$

in which C has been expressed in normalized units to simplify the expression, A is the average dye concentration after photobleaching, and a is the spatial frequency of the pattern, defined as $a = 2\pi/p$, where p is the pitch or repeat distance of the striped pattern. The terms in eq 2 represent the Fourier components of a square wave.

The solution to eq 1 with initial conditions of eq 2 is given by

$$C(x,t) = A + e^{-Da^2t}\sin(ax) + \tfrac{1}{3}e^{-9Da^2t}\sin(3ax) + \tfrac{1}{5}e^{-25Da^2t}\sin(5ax) + \ldots \tag{3}$$

The observed fluorescence intensity is proportional to the concentration integrated over the illuminated portion of the square wave pattern.

$$I(t) \propto \int_{\pi/a}^{2\pi/a} C(x,t)\,\mathrm{d}x \tag{4}$$

$$I(t) \propto \pi A - 2e^{-Da^2t} - \tfrac{2}{9}e^{-9Da^2t} - \ldots \tag{5}$$

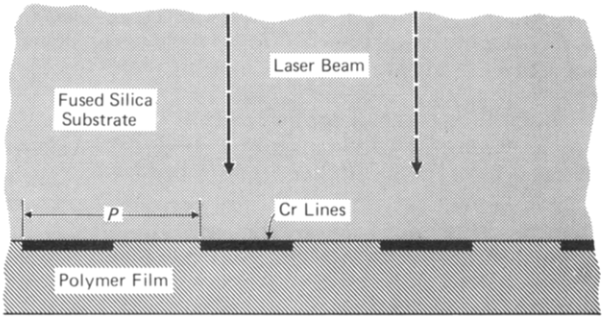

Figure 1. Diagram of polymer film sample on shadow mask. The polymer film thickness is 1.0 μm. The pattern period $p = 1.0$ μm.

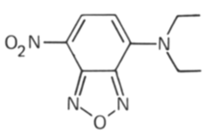

Figure 2. Chemical structure of the fluorescent dye 7-(diethylamino)-4-nitrobenz-2-oxa-1,3-diazole.

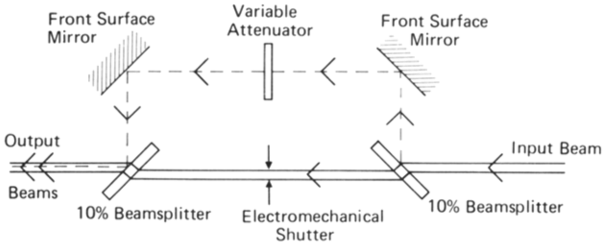

Figure 3. Schematic diagram of laser modulator. Each of the beam splitters has one surface which reflects 10% of the light at 45°. The other surface is coated to reflect less than 1%. The light is s-polarized at all reflections. The attenuator varies in optical density from 0.5 to 2.5.

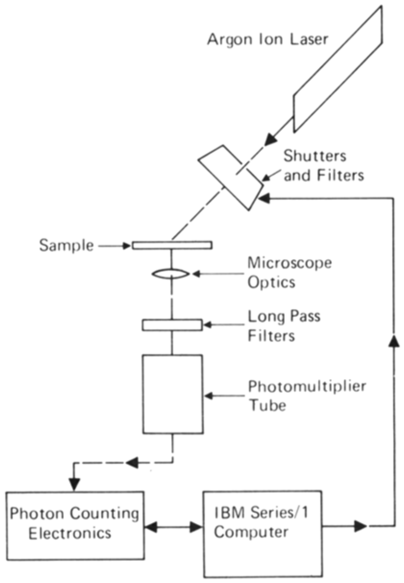

Figure 4. Block diagram of apparatus for fluorescence redistribution after pattern photobleaching.

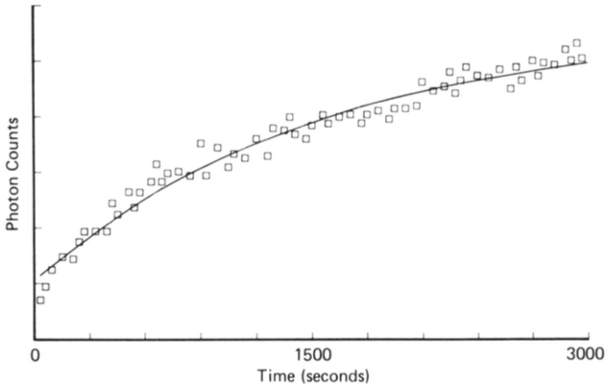

Figure 5. Graph of fluorescence intensity vs. time for photobleached sample. The squares are experimental points. The solid line is the best fit to a single exponential.

In reality, the pattern of light on the sample is not a perfect square wave due to fundamental diffraction limitations. This leads to a reduction in the amplitude of the higher frequency terms in eq 2 and 3. Thus the third and succeeding terms in eq 5 are made smaller with respect to the second term. Since these terms, which correspond to the higher frequency components, decay much more rapidly than the fundamental term, they become insignificant shortly after the bleaching burst and may be neglected in the analysis of the experimental data. The observed fluorescence intensity can be fit to a single-exponential recovery curve, which has a time constant $\tau = 1/Da^2$.

Experimental Section

The pattern mask was made by X-ray lithography on a 2.5-cm-diameter fused-silica optical window. The mask consisted of 700-Å-thick vapor-deposited chromium in a pattern of 0.50-μm-wide lines spaced 0.50 μm apart, the lines covering a 1-mm-square area. The polymer solution was filtered through a 5-μm pore filter (Millipore MITEX) and spin coated directly onto the mask at 2500 rpm at room temperature (24 °C). The resulting film was measured to be 1.00 ± 0.05 μm thick on a Tencore Alpha Step (see Figure 1).

The polymer solution consisted of 6.5% by weight poly(methyl methacrylate) (Elvacite 2041) in chlorobenzene to which fluorescent dye had been added. Elvacite 2041 is an atactic PMMA with $M_w = 500\,000$ and $M_n = 160\,000$. The dye, 7-(diethylamino)-4-nitrobenz-2-oxa-1,3-diazole (see Figure 2), was added in an amount equal to 0.02% by weight of the polymer. The dye was made by reaction of NBD chloride (Pierce 26030) with diethylamine and purified by thin-layer chromatography.

The light source was a Spectra Physics Model 165-09 argon ion laser producing 500 mW of output at 488 nm. An assembly of beam splitters, attenuators, and shutters was used to provide the collinear high-power bleach and low-power observation beams (see Figure 3). The 1-mm-diameter beams were incident on the sample at an angle of 45°, p polarized. The metal lines in the mask were aligned parallel to the plane of incidence. Light power at the sample was 200 mW for bleaching and 200 μW for observation. Light from the sample was collected by the optical system of an inverted microscope with a 20×, numerical aperture = 0.5 objective, filtered to remove scattered light at the excitation wavelength, and focused onto the photocathode of an RCA C31034-A photomultiplier tube. A Princeton Applied Research Models 1112 and 1121 photon counting system was operated in the chopped mode (automatic background subtraction) to measure fluorescence intensity. The photon count rate was on the order of 10^5 per second. An IBM Series/1 computer was used to control the apparatus and collect the data. Figure 4 shows a diagram of the apparatus.

Results

Figure 5 is a graph of fluorescence intensity vs. time after the bleach pulse for a single measurement. The squares represent the experimental data and the solid line is a least-squares fit to the data of a single-exponential recovery curve. The time constant for this curve is 1551 s. Given that the pattern period is 1.0 μm, the diffusion coefficient is $D = 1.63 \times 10^{-13}$ cm^2/s. The reproducibility of the measurements was limited by the reproducibility of the samples. The variation in diffusion coefficient among different samples was about 25%, most likely reflecting variations in solvent content. Note the deviation from single-exponential behavior at very short times (the first two points) due to the decay of the higher spatial frequency components of the pattern. This analysis assumes that the diffusion coefficient is uniform throughout the thickness of the film. The single-exponential nature of the recovery curve indicates that this assumption is approximately correct. The measured diffusion coefficient is an average value.

For this measurement, the bleach burst had a duration of 300 ms, sufficient to reduce the fluorescence intensity by 40%. The recovery was 60% of the amount predicted for a perfect square wave pattern. The sample was illuminated for observation of fluorescence intensity for 1 s out of every 30 s.

Discussion

When a thin film of a glass-forming polymer is cast from solvent, the solvent evaporates rapidly from the film until the glass transition temperature is below the casting temperature, at which point the rate of solvent evaporation decreases rapidly. For PMMA cast from chlorobenzene at 25 °C, the film retains about 20% solvent by weight immediately after casting. The solvent content decays to about 10% with a time constant of 47 h and then further decays much more slowly.[15] These measurements were made on films between 1 and 2 h after casting and thus represent samples which are below the glass transition and contain about 18% solvent.

The diffusion coefficient measured here is several orders of magnitude higher than would be expected for a molecule of this size in solvent-free glassy PMMA.[16] This relatively fast diffusion is a result of the substantial solvent content of the films. Thus this method can be used to measure slow diffusion in glassy polymers as a function of solvent content. Although this technique can be pushed to measure extremely slow diffusion, the convenient range of application lies between 10^{-8} and 10^{-14} cm^2/s. It is thus also applicable to measurements of diffusion of polymer molecules in solids, melts and concentrated solutions. Efforts are under way to synthesize labeled molecules for measurements in these systems.

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References and Notes

(1) Klein, J. *Macromolecules* **1978**, *11*, 852–858.
(2) Daoud, M.; de Gennes, P. G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1971–1981.
(3) Hervet, H.; Léger, L.; Rondelez, F. *Phys. Rev. Lett.* **1979**, *42*, 1681–1684.
(4) Klein, J.; Briscoe, B. J. *Proc. R. Soc. London, Ser. A* **1979**, *365*, 53–73.
(5) Gilmore, P. T.; Falabella, R.; Laurence, R. L. *Macromolecules* **1980**, *13*, 880–883.
(6) Nyström, Bo; Roots, Jaan *J. Macromol. Sci., Rev. Macromol. Chem.* **1980**, *C19*, 35–82.
(7) Ueberreiter, K. In "Diffusion in Polymers"; Crank, J., Park, G. S., Eds.; Academic Press: New York, 1968; pp 219–257.
(8) Tu, Y. O.; Ouano, A. C. *IBM J. Res. Dev.* **1977**, *21*, 131–142.
(9) Smith, B. A.; McConnell, H. M. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 2759–2763.
(10) Smith, L. M.; Smith, B. A.; McConnell, H. M. *Biochemistry* **1979**, *18*, 2256–2259.
(11) Smith, L. M.; Parce, J. W.; Smith, B. A.; McConnell, H. M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 4177–4179.
(12) Smith, B. A.; Clark, W. R.; McConnell, H. M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 5641–5644.
(13) Petty, H. R.; Smith, L. M.; Fearon, D. T.; McConnell, H. M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6587–6591.
(14) Berens, A. R. *J. Vinyl Technol.* **1979**, *1*, 8–13.
(15) Ouano, A. C. IBM Research Report RJ3203 (39129), 1981. Copies may be requested from IBM Research, Distribution Services, P.O. Box 218, Yorktown Heights, NY 10598.
(16) Berens, A. R.; Hopfenberg, H. B. "Diffusion of Organic Vapors at Low Concentrations in Glassy PVC, Polystyrene, and PMMA", presented at the AIChE National Meeting in Houston, Apr 1981 (in press, *J. Membr. Sci.*).