Picosecond excimer fluorescence spectroscopy: applications to local motions of polymers and polymerization monitoring

F. W. Wang and R. E. Lowry
Polymers Division, National Bureau of Standards, Gaithersburg, Maryland 20899, USA

and R. R. Cavanagh
Molecular Spectroscopy Division, National Bureau of Standards, Gaithersburg, Maryland 20899, USA

(*Received 8 February 1985*)

The local motions of α,ω-bis-(1-pyrene)alkanes and pyrene-labelled poly(methyl methacrylate) polymers in solution were characterized by picosecond excimer fluorescence spectroscopy. The experimental results showed that 1,3-bis-(1-pyrene)propane and 1,10-bis-(1-pyrene)decane have similar local motions that bring two pyrene groups together to form excimers. Further, poly(1-pyrenylmethyl methacrylate) and a copolymer of methyl methacrylate and 1-pyrenylmethyl methacrylate in solution were found to have similar local motions that lead to excimer formation. In addition, the viscosity change during the polymerization of methyl methacrylate was monitored by measuring with picosecond fluorimetry the fluorescence lifetime of a trace amount of 1,3-bis-(1-pyrene)propane dissolved in methyl methacrylate.

(Keywords: excimer; fluorescence spectroscopy; local motions; picosecond light source; polymerization; time-resolved fluorescence)

INTRODUCTION

An excimer is formed by the association of an excited molecule with another molecule in its ground state. Such an excimer gives off a broad structureless fluorescence which has longer wavelengths than the fluorescence of the isolated excited molecule. Excimers may also be formed intramolecularly from molecules carrying excimer-forming groups. For example, excimer fluorescence has been observed in dilute solutions of pyrene-labelled alkanes such as 1,3-bis-(1-pyrene)propane and 1,10-bis-(1-pyrene)decane[1].

At low enough temperature in a solution of smaller excimer-forming species, the extent of excimer formation depends on the rate constant for the diffusion-controlled reaction of an excited monomer and a monomer in the ground state to form an excimer. If the excimer-forming species are covalently attached to a polymer chain, this rate constant will in addition depend on the local motions of the polymer. Therefore, we can learn about these local motions by measuring the excimer fluorescence of polymers carrying excimer-forming groups.

In our previous papers[2,3], we have used the steady-state excimer fluorescence technique to characterize the local motions of polymers and to monitor the polymerization of methyl methacrylate. We present here the results of our efforts to characterize by picosecond excimer fluorescence spectroscopy the local motions of α,ω-bis-(1-pyrene)alkanes and pyrene-labelled poly(methyl methacrylate) polymers. Furthermore, we describe here the results of our work to monitor the polymerization of methyl methacrylate by picosecond excimer fluorescence spectroscopy.

EXPERIMENTAL

Pyrene-labelled alkanes

1,3-bis-(1-pyrene)propane and 1,10-bis-(1-pyrene)decane (both from Molecular Probes, Inc.*) were used without further purification.

Polymers

Poly(1-pyrenylmethyl methacrylate) and the copolymer of 1-pyrenylmethyl methacrylate (πMMA) and methyl methacrylate (MMA) were prepared by free radical polymerization in benzene at 60°C with the use of azobisisobutyronitrile as a catalyst. The mole fraction of 1-pyrenylmethyl methacrylate in the copolymer, hereafter referred to as π-PMMA (3%), as determined by u.v. absorption spectroscopy was 0.032. *Figure 1* gives the chemical structure of the copolymer. The homopolymer of πMMA was found to be soluble in chloroform but apparently not soluble at room temperature in acetonitrile, methylene chloride, benzene, butanone, ethyl acetate, amyl acetate, and butyrolactone.

Solvents

Ethyl acetate and chloroform (Burdick and Jackson

---

* Certain commercial equipment, instruments or materials are identified in this paper in order to specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

0032-3861/85/111657-05$03.00

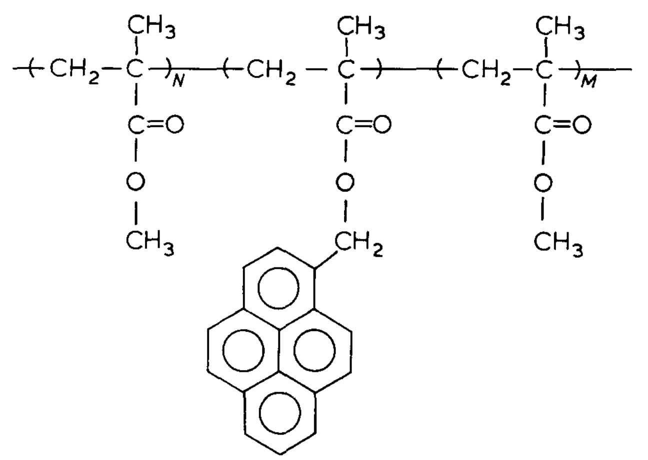

Figure 1 Chemical structure of the copolymer of 1-pyrenylmethyl methacrylate and methyl methacrylate

Laboratories, 'Distilled in Glass') were used without further purification.

Steady-state fluorescence measurements

Uncorrected fluorescence spectra were taken on a spectrofluorimeter equipped with a thermostatically controlled sample holder and a reference detector to correct for variation in the lamp intensity. The concentrations of pyrene-labelled alkanes in solutions were 5.2×10^{-5} mol l^{-1}. All solutions were degassed by repeated freeze-pump-thaw cycles. All the spectra were taken with frontal illumination at an excitation wavelength of 343 nm, and with bandpasses of 10 nm and 5 nm for the excitation monochromator and the emission monochromator respectively.

Time-resolved fluorescence measurements

The time-resolved fluorescence data were obtained using the third harmonic of a passively mode locked NdYAG laser at 355 nm to excite the specimens. The resultant single shot time-resolved fluorescence traces were monitored using a streak camera. The temporal response of the streak camera was calibrated on its different sweep speeds using the second harmonic of the laser (FWHM = 28 ps) and a set of air spaced etalons[4]. The output of the streak camera was imaged onto a 512 element silicon intensified target (SIT) which was subsequently read by a computer. Averaging of fluorescence decay traces for each sample was accomplished with the computer, rather than integrating on the SIT. Band pass filters at 410 nm (FWHM = 14.2 nm) and 510 nm (FWHM = 13.6 nm) were inserted between the sample and the collection optics of the streak camera in order to spectrally resolve monomer and excimer emission.

Monitoring methyl methacrylate polymerization

The inhibitor, *p*-methoxyphenol, was removed from 100 ml of methyl methacrylate (MMA) by washing twice with an aqueous solution containing 1% sodium hydroxide and 25% sodium carbonate, once with a saturated salt solution and twice with water. The washed monomer was dried by passing it through anhydrous calcium sulphate and storing it over molecular sieve 4A. The dried monomer was filtered, outgassed and then stirred at 50°C with 6 mg of 2,2'-azobis-(2-methylpropionitrile) (AIBN), recrystallized from ethanol. When the mixture became more viscous, it was cooled to 25°C and 50 ml MMA was distilled into a pre-evacuated storage tube and sealed off *in vacuo*. The monomer was stored in the dark at −8°C prior to use.

Sufficient monomer for polymerizations was distilled into a pre-evacuated, valved transfer bulb on a vacuum line. Polymerization tubes (9 mm O.D., Pyrex), each containing AIBN and 1,3-bis-(1-pyrene)propane in chloroform, were attached to the line with tapered joints. The molarities of pyrene groups and AIBN were $(2\text{–}4) \times 10^{-6}$ M and 10^{-2} M, respectively. The chloroform was removed to a trap and replaced in each tube by an equal volume of MMA. After sealing off under vacuum, the tubes, each 90 mm in length and containing 1.2 ml solution, were stored in liquid nitrogen before use.

Polymerization was carried out in half-hour intervals at 55°C. Between intervals, the tubes were rapidly cooled to 22°C, the contents mixed when possible and analysed in a thermostatically controlled spectrofluorimeter or by time-resolved fluorescence spectroscopy. Changes in appearance of the polymerizing mass were noted and the tube was returned to the 55°C bath within 20 min. The degree of conversion was determined by drying and then weighing the polymer after the unreacted monomer was removed by extraction.

RESULTS AND DISCUSSION

The fluorescence spectra of 1,3-bis-(1-pyrene)propane and 1,10-bis-(1-pyrene)decane in ethyl acetate at 22.0°C are shown in *Figure 2*, in which the spectral intensities have been normalized to a common excimer fluorescence quantum yield. The spectra, showing structured violet fluorescence emission bands at 377 nm and broad structureless blue fluorescence with maxima near 480 nm, are similar to the fluorescence spectra of concentrated pyrene solutions[5] and also similar to the spectra of the dilute solutions of pyrene-labelled poly(methyl methacrylate) polymers[2]. The structured bands are due to the emission from excited, isolated pyrenyl groups, hereafter referred to as monomers, while the structureless bands are due to the emission from intramolecularly formed pyrenyl excimers, hereafter referred to as excimers.

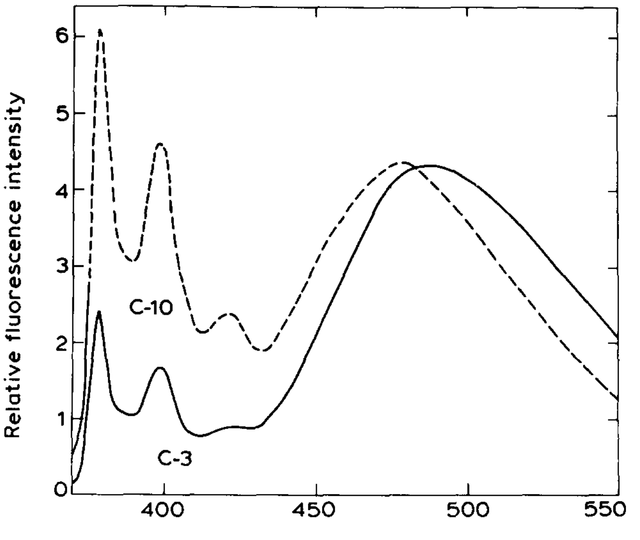

Figure 2 Uncorrected fluorescence spectra of 1,3-bis-(1-pyrene)-propane (——) and 1,10-bis-(1-pyrene)decane (– – – –) in ethyl acetate at 22.0°C. The excitation wavelength was 343 nm

Local motions

Figure 3 gives for a dilute solution of poly(1-pyrenylmethyl methacrylate) [π-PMMA] in chloroform the intensity of pyrene-excimer fluorescence at 510 nm as a function of time. Here, each 100 channels represents 6.85 ns and the number of counts is proportional to the fluorescence intensity. The most striking feature seen here is the absence of a rise-time for the excimer fluorescence. In other words, there is a nearly instantaneous rise of the excimer fluorescence intensity to almost its maximum value. This nearly instantaneous rise is surprising, since pyrene groups are thought to be repulsive toward one another in the ground state. One plausible explanation is that the pyrene groups of an isolated π-PMMA molecule in chloroform are very close to one another. This proximity of the pyrene groups will allow a rapid migration of the electronic excitation to the sites where two pyrene groups are almost in the proper orientation for excimer formation. The nearly instantaneous rise is followed by a slower and smaller rise, and finally an exponential decay with a lifetime of 36 ns. This slower and smaller rise can be attributed to the local motions of two pyrene groups toward each other to form a pyrene excimer.

Figure 4 gives, for a dilute solution of 1,3-bis-(1-pyrene)propane (C-3) in ethyl acetate and a dilute solution of 1,10-bis-(1-pyrene)decane (C-10) in ethyl acetate, the intensity of pyrene-excimer fluorescence at 510 nm as a function of time. In contrast to the excimer fluorescence intensity for πPMMA, the fluorescence intensity for each of the solutions rises much more slowly, reaches a plateau in about 14 ns, and finally decays. This indicates that for both C-3 and C-10, the motions of two pyrene groups toward each other precede the excimer formation. The near coincidence of the curves for C-3 and C-10 suggests that, despite the difference of seven methylene units, C-3 and C-10 have the same kind of local motions that bring pairs of pyrene groups together in about 14 ns to form pyrene excimers.

Figure 5 gives for a dilute solution of the copolymer π-PMMA (3%) in ethyl acetate the intensity of pyrene-excimer fluorescence at 510 nm as a function of time. Here, we see a rapid rise of the fluorescence intensity in about 5 ns, much longer than the rise-time for the solution of π-PMMA. This rapid rise is followed by a plateau region of about 14 ns when the decay of pyrene excimers is compensated by the diffusion-controlled formation of pyrene excimers through local motions. The decrease in the intensity of excimer fluorescence occurs about 20 ns after the excitation.

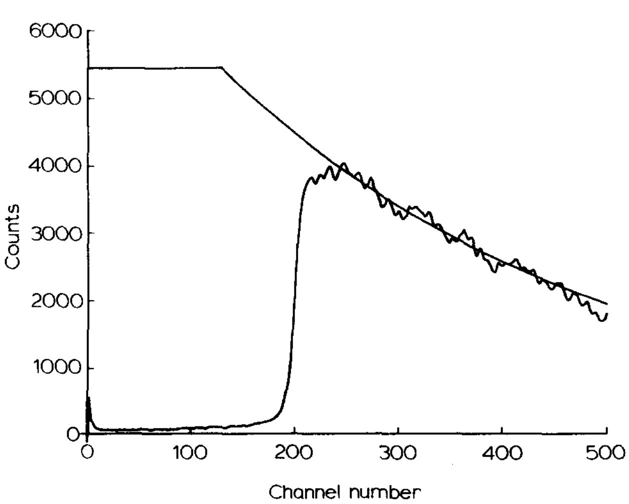

Figure 3 Time-resolved excimer fluorescence of poly(1-pyrenylmethyl methacrylate) in chloroform

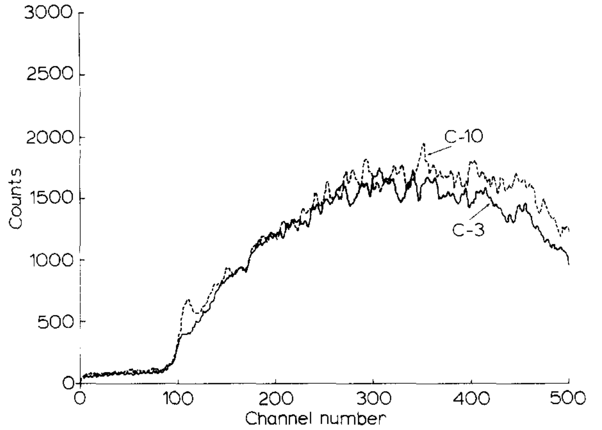

Figure 4 Time-resolved excimer fluorescence for a solution of 1,3-bis-(1-pyrene)propane in ethyl acetate and for a solution of 1,10-bis-(1-pyrene)decane in ethyl acetate

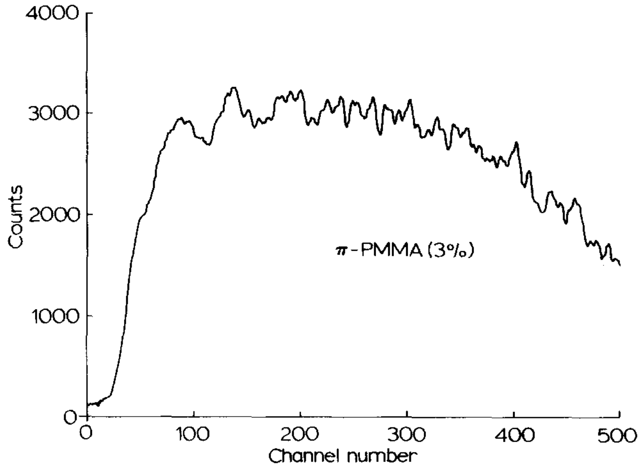

Figure 5 Time-resolved excimer fluorescence of a pyrene-labelled poly(methyl methacrylate) polymer in ethyl acetate

Figure 6 gives for the dilute solution of π-PMMA in chloroform the intensity of pyrene-monomer fluorescence at 410 nm as a function of time. The decay curve is well represented by the sum of two exponentials, with lifetimes of 1.7 ns and 19 ns. The fast component accounts for most of the decay of the initial fluorescent intensity. This predominance of the fast-decaying component is consistent with the nearly instantaneous rise of the excimer fluorescence intensity observed in *Figure 3*.

Figure 7 gives for the dilute solution of copolymer π-PMMA (3%) in ethyl acetate the intensity of pyrene-monomer fluorescence at 410 nm as a function of time. Here again, the decay curve has two components, but the slower-decaying component with a lifetime of 20 ns dominates. The close agreement of this time constant with the one for π-PMMA in chloroform suggests that the homopolymer and the copolymer in solution have the same kind of local motions that bring two pyrene groups together to form excimers.

Figures 8 and *9* give for the dilute solutions C-3 and C-10 in ethyl acetate the intensity of pyrene-monomer fluorescence at 410 nm as a function of time. We see here

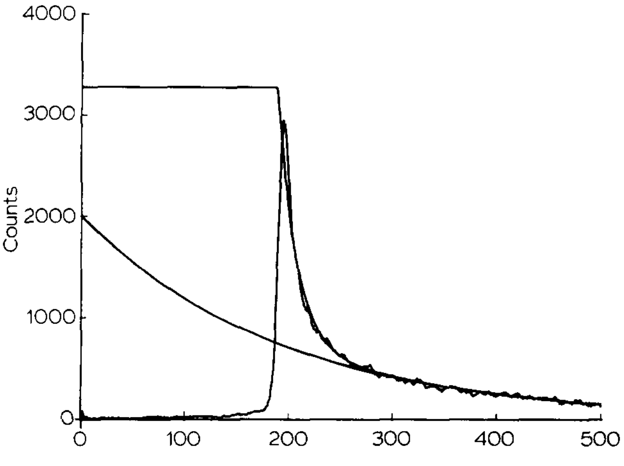

Figure 6 Time-resolved monomer fluorescence of poly(1-pyrenylmethyl methacrylate) in chloroform

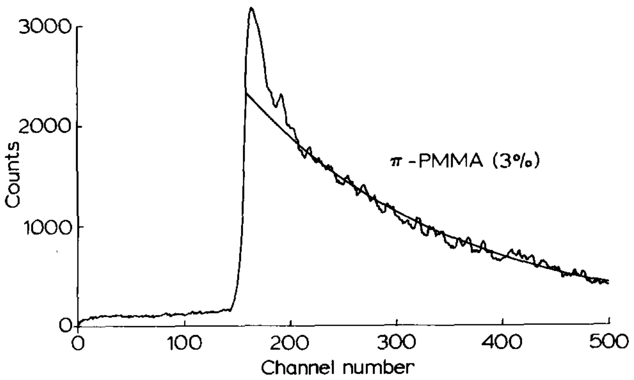

Figure 7 Time-resolved monomer fluorescence of a copolymer of 1-pyrenylmethyl methacrylate and methyl methacrylate in ethyl acetate

that for these solutions the contribution of the fast-decaying component is very small. The lifetimes of the slower-decaying components are 12 ns and 10 ns for C-3 and C-10, respectively. The close agreement of these lifetimes suggests that C-3 and C-10 in ethyl acetate have the same kind of local motions that bring two pyrene groups together to form excimers.

Polymerization monitoring

The intensity of pyrene-excimer fluorescence depends on the viscosity of the medium because a pyrene excimer is formed by the diffusion-controlled reaction of an excited pyrene group and a pyrene group in the ground state. In a previous paper[3], we have shown that for pyrene-labelled alkanes, the fluorescence intensity ratio F_M/F_D (where F_M and F_D are the fluorescence intensities of the monomers at 377 nm and that of excimers at 488 nm) varies linearly with the solvent viscosity up to 4 cP.

Since the F_M/F_D ratio of the pyrene-labelled alkanes and the πMMA–MMA copolymer[2] depends on the viscosity of the medium, they can act as probes to monitor the viscosity change taking place during polymerization. *Figure 10* shows the change in $\log(F_M/F_D)$ of 1,3-bis-(1-pyrene)propane as a function of the degree of conversion. $\text{Log}(F_M/F_D)$ increases gradually, but at a readily measurable rate, up to 40% conversion and then increases rapidly as the sample becomes highly viscous.

Figure 11 shows, for 1,3-bis-(1-pyrene)propane, the change in the F_M/F_D ratio and the lifetime of pyrene-monomer fluorescence as a function of polymerization time. Here again, the F_M/F_D ratio and the monomer lifetime increase gradually up to about 3.5 h after the start of the polymerization and then increase rapidly as the samples become very viscous.

The observed increase in the monomer lifetime with polymerization is directly related to the time dependence observed for the excimer emission in *Figure 4* and the monomer emission in *Figure 8*. If excimer formation is inhibited in any way during the polymerization, then fluorescence from excited monomers will no longer reflect decay paths which require passage through the excimer. For instance, if the increase in the ratio F_M/F_D were simply due to reduction in quantum yield of the excimer, then the monomer lifetime would not change. The observed change in monomer decay rate demonstrates that the change in F_M/F_D cannot be attributed to a quantum yield effect. The increase in monomer lifetime reflects the reduced ability of the pyrene to reorient into a configuration favourable for excimer generation as the reaction proceeds. Hence, both the ratio F_M/F_D and the monomer fluorescence lifetime reflect reaction dependent changes in local motions which accompany excimer formation.

Since our measurements involve the life-time or the ratio of the fluorescence intensities at two wavelengths, they are insensitive to the geometry of the samples. This

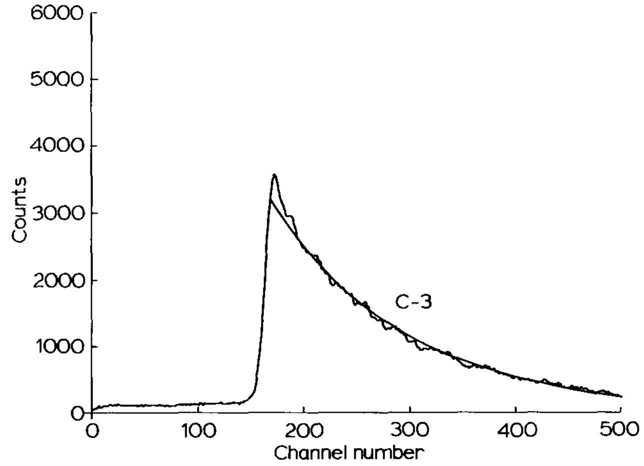

Figure 8 Time-resolved monomer fluorescence of 1,3-bis-(1-pyrene)-propane in ethyl acetate

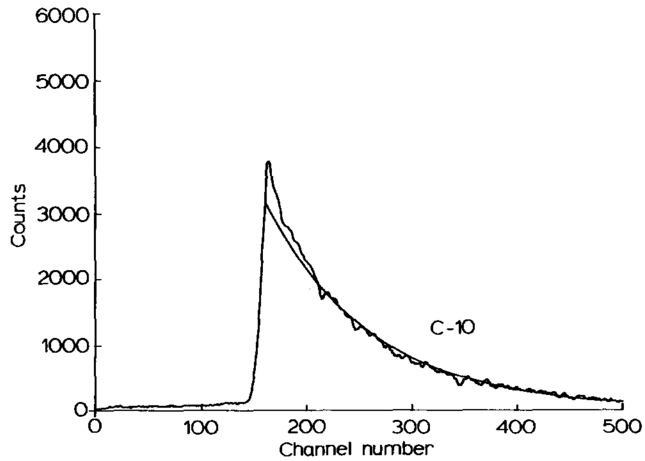

Figure 9 Time-resolved monomer fluorescence of 1,10-bis-(1-pyrene)-decane in ethyl acetate

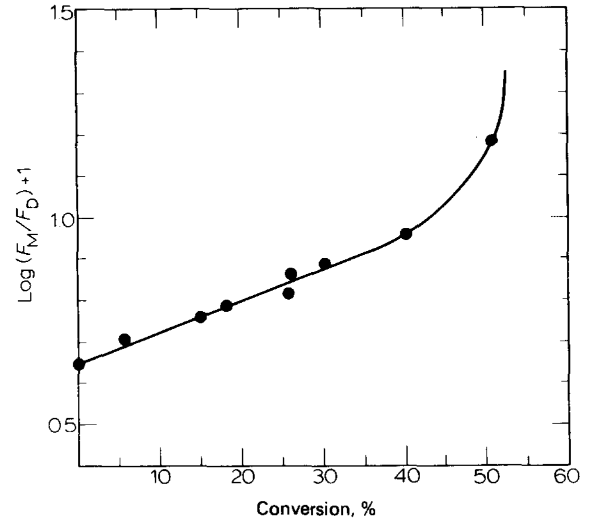

Figure 10 Plot of the intensity ratio $\log(F_M/F_D)$ against percentage conversion. F_M and F_D are defined in the text

insensitivity allows us to monitor the polymerization of samples with irregular geometry. For example, we have successfully monitored the polymerization of a methyl methacrylate sample containing 8% by volume of Pyrex fibreglass[3].

CONCLUSION

We have described in this paper the local motions of α,ω-bis-(1-pyrene)alkanes and pyrene-labelled poly(methyl methacrylate) polymers in solution. We have also described a novel method to monitor polymerization reactions by measuring the lifetime or the excimer and the monomer fluorescence of a minute amount of a fluorescence probe dissolved in a polymerizing medium. Since the method is insensitive to the sample geometry, it can be readily adopted for *in situ* monitoring of the curing of composite structures in the factory environment.

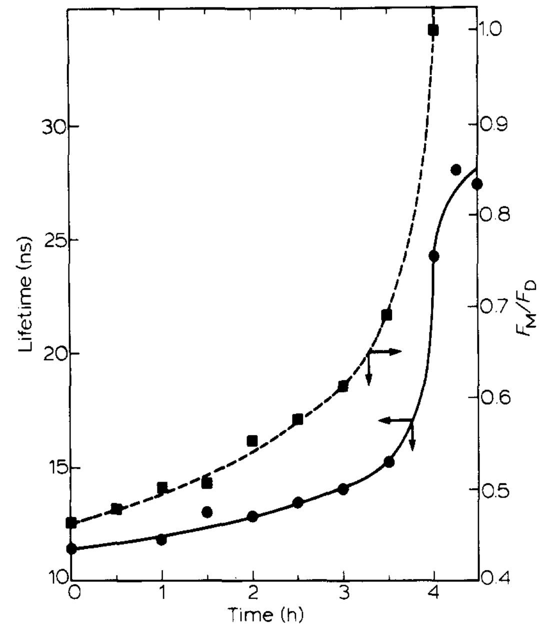

Figure 11 Plots of the lifetime of monomers and the intensity ratio F_M/F_D against the polymerization time

ACKNOWLEDGEMENT

This work was partially supported by the U.S. Army Research Office through Contract MIPR ARO 111-84.

REFERENCES

1 Zachariasse, K. A. and Kuhnle, W. Z. *Phys. Chem. NF* 1976, 101
2 Wang, F. W. and Lowry, R. E. *Polymer* 1985, **26**, 1046
3 Wang, F. W., Lowry, R. E. and Grant, W. H. *Polymer* 1984, **25**, 690
4 Campillo, A. J. and Shapiro, S. L. *IEEE J. Quantum Electronics* 1983, **QE-19**, 585
5 Birks, J. B. 'Photophysics of Aromatic Molecules', Wiley-Interscience, New York, 1970