Novel excimer fluorescence method for monitoring polymerization: 1. Polymerization of methyl methacrylate

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An excimer is formed by the association of an excited molecule with another molecule in its ground state. Such an excimer is characterized by a broad structureless fluorescence which is shifted to longer wavelengths compared to the fluorescence spectrum of the isolated molecule. Intramolecular excimer fluorescence has been observed in solutions of pyrene-labelled alkanes such as 1,3-bis-(1-pyrene)propane and 1,10-bis-(1-pyrene)decane.

We have measured the solvent-viscosity dependence of the intensity ratio F_M/F_D for solutions of these pyrene-labelled alkanes in mixed solvents made of ethyl acetate and glycerol tripropionate. Here F_M and F_D are, respectively, the fluorescence intensity of the unassociated pyrene groups and that of the intramolecularly formed pyrene excimers. We have found that for each of the two pyrene-labelled alkanes, the ratio F_M/F_D increases with the increase in solvent viscosity. Further, we have shown that by adding a trace amount of 1,3-bis-(1-pyrene)propane or 1,10-bis-(1-pyrene)decane to a polymerizing system, we can measure the ratio F_M/F_D to monitor *in situ* the polymerization reaction.

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].

Although 1,3-bis-(1-pyrene)propane has been used to preliminary results of our efforts to use pyrene-labelled micelles[2], there has been no report of the use of pyrene-labelled alkanes for *in situ* monitoring of polymerization reactions, to the best of our knowledge. We present here preliminary results of our efforts to use pyrene-labelled alkanes for *in situ* monitoring of the polymerization of methyl methacrylate.

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.

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* 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.

Copolymer

The copolymer of 1-pyrenylmethyl methacrylate (πMMA) and methyl methacrylate (MMA) was 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 as determined by u.v. absorption spectroscopy was 0.057. The limiting viscosity number of the copolymer in ethyl acetate at 20.0°C was 47 cm^3 g^{-1}.

Solvents

Ethyl acetate (Burdick and Jackson Laboratories, 'Distilled in Glass') was used without further purification. Glycerol tripropionate was found to have an acid content of 2×10^{-6} Eq g^{-1} and was purified according to the following procedures. A 350 cm^3 portion of glycerol tripropionate was washed twice with 30% aqueous K_2CO_3 and thrice with water. The volatile components were distilled away from the washed liquid at room temperature and reduced pressure whereupon the washed liquid became clear. The washed liquid was then dried over molecular sieves (Linde 4A) *in vacuo*, filtered, and distilled without a column under reduced pressure. After about 15% of the liquid was distilled away, distillate was collected at ~173°C/20 mm until 75% of the liquid was collected. The distillate was further purified by distilling *in vacuo* with the use of a 6 inch Vigreux column.

Densimetry

The densities of the purified glycerol tripropionate and a 1:1 by weight mixture of glycerol tripropionate and ethyl acetate were determined at 22.0°C with a

calibrated pycnometer. The density of ethyl acetate at 22.0°C was interpolated from the densities at 20°C and 25°C^3. The densities of other mixtures of ethyl acetate and glycerol tripropionate were estimated by linear interpolation.

Viscometry

The viscosity of ethyl acetate at 22.0°C was interpolated from viscosities at 15.0°C and 25.0°C^3. The kinematic viscosities of some mixtures of ethyl acetate and glycerol tripropionate were determined at 22.0°C with Cannon–Ubbelohde viscometers. The viscosities of other mixtures were estimated graphically from the plot of the square root of the viscosity against the weight fraction of glycerol tripropionate.

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.

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% NaOH and 25% Na_2CO_3, once with a saturated NaCl 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 methanol). When the mixture gave evidence of polymerization, it was cooled to 25°C and 50 ml MMA was distilled into a pre-evacuated storage tube containing 50 mg t-butyl hydroxytoluene and sealed off *in vacuo*. 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 a pyrene-labelled alkane or the πMMA–MMA copolymer in chloroform, were attached to the line with tapered joints. The molarities of pyrene groups and AIBN were $(2–4) \times 10^{-6}$ 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. Changes in appearance of the polymerizing mass were noted and the tube was returned to the 55°C bath within 20 min.

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 1*, in which the spectral intensities have been normalized to a common excimer fluorescence quantum yield. The spectra, showing structural 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[4]. 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.

The maximum of the excimer emission for 1,10-bis-(1-pyrene)decane occurs at a shorter wavelength than that for 1,3-bis-(1-pyrene)propane. Zachariasse and Kuhnle[1] have also observed this blue shift in methylcyclohexane solutions of α,ω-bis-(1-pyrene)alkanes with 2, 4, 5, 6, 8 and 9 methylene groups. They have attributed this blue shift to the inability of the pyrene groups in these alkanes to reach an optimal intramolecular sandwich configuration.

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. *Figure 2* shows the solvent-viscosity dependence of the F_M/F_D ratio for solutions of 1,3-bis-(1-pyrene)propane in mixed solvents made of ethyl acetate and glycerol tripropionate. Here F_M and F_D are, respectively, the fluorescence intensity of the monomers at 377 nm and that of excimers at 488 nm. *Figure 2* also shows the solvent viscosity dependence of the F_M/F_D ratio for solutions of 1,10-bis-(1-pyrene)decane. For these solutions, F_M is again the fluorescence intensity at 377 nm but F_D is the fluorescence intensity at 478 nm. For both pyrene-labelled alkanes, the F_M/F_D ratio 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[5] depends on the viscosity of the medium, they can act as probes to monitor the viscosity change taking place during poly-
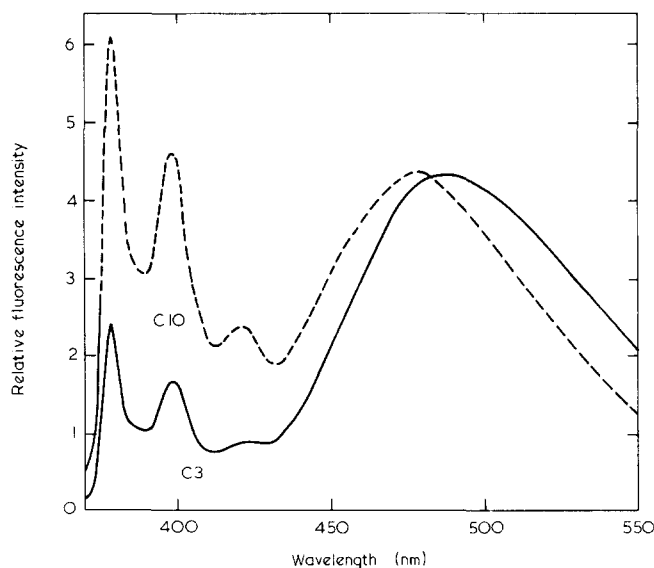

Figure 1 Uncorrected fluorescence spectra of 1,3-bis-(1-pyrene)propane (———) and 1,10-bis-(1-pyrene)decane (– – –) in ethyl acetate at 22.0°C. The excitation wavelength was 343 nm
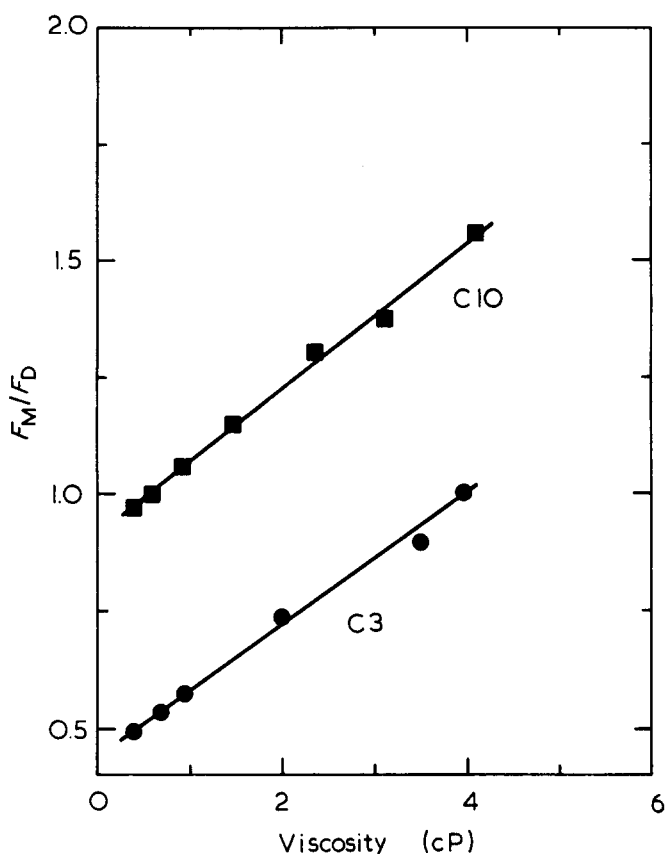
Figure 2 Plots of F_M/F_D as a function of solvent viscosity for solutions of 1,3-bis-(1-pyrene)propane (●) and 1,10-bis-1-pyrene)decane (■). Symbols are defined in the text

Figure 3 Plots of $\log(10F_M/F_D)$ as a function of polymerization time for fluorescence probes 1,10-bis-(1-pyrene)decane (C-10), πMMA–MMA copolymer (π-PMMA) and 1,3-bis-(1-pyrene) propane with and without fibreglass in MMA (C-3 and C-3(Glass)) Symbols are defined in the text

merization. *Figure 3* shows the change in the F_M/F_D ratio as a function of polymerization time for each of the polymerizing methyl methacrylate samples containing the πMMA–MMA copolymer or one of the pyrene-labelled alkanes. For all the samples, the F_M/F_D ratio increases gradually, but at a readily measurable rate, up to 3 h after the start of the polymerization and then increases rapidly as the samples become highly viscous.

Since our measurements involve the ratio of the fluorescence intensities at two wavelengths, they are insensitive to the geometry of the samples. This 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, as shown in *Figure 3*. The F_M/F_D ratio for the polymerizing system containing fibreglass increases faster than the ratios for the three other polymerizing systems. We have not investigated whether this faster
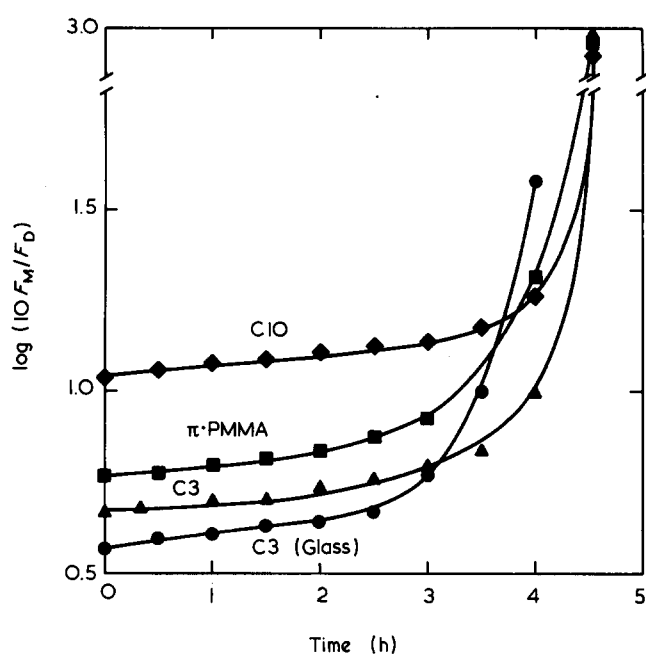
increase is due to the adsorption of the probe on the fibreglass surfaces or due to the higher local concentration of AIBN caused by incomplete mixing.

CONCLUSIONS

We have described in this paper a novel method to monitor polymerization reactions by measuring 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.

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