A polymer-based optical switch

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Changes in the polarized components of the fluorescence have been measured as suspensions of dye-tagged poly(tetrafluoroethylene) latex particles have been subjected to electric pulses. The data indicate a potential use of the phenomenon for a new class of multicoloured, fast, optical switches, based on electroactive polymers.

(Keywords: fluorescence; electro-optics; poly(tetrafluoroethylene))

INTRODUCTION

In 1980, we reported[1] a novel mechanism based upon dye-tagged particles of the mineral sepiolite, which could form the basis of a coloured optical switch. The key to the mechanism lay in three principal factors. Firstly, the morphology of the mineral particles was highly anisodiametric. In this case they were long, thin needles. The associated crystallographic structure resulted in surface channels running parallel with the major axis of the particles. Into these channels, planar ring fluorescent compounds could apparently be physisorbed, but in a highly restrained manner so as to be directionally ordered parallel with the long axes of the needles. Secondly, fluorescence is a two-fold optical process that involves the absorption of incident light whose electric vector direction ($\bar{p}$) can be resolved at least partially parallel to an absorption transition moment ($\bar{a}$) associated with the fluorophore structure. The absorption, and hence the associated fluorescent emission, can thus be controlled by using linearly polarized incident light, and aligning fluorophores so that $\bar{a}$ is parallel to $\bar{p}$ for optimized fluorescence or $\bar{a}$ is perpendicular to $\bar{p}$ for minimal fluorescence. This is the basis of the optical switch. Thirdly, the required fluorophore alignment was achieved using an electric field, not primarily to align isolated fluorescent molecules (which would require an inordinately high electric field amplitude), but rather to align the tagged sepiolite substrate particles which were themselves held in dilute suspension. In this manner, a switching principle was demonstrated whose speed was controlled by the rotary diffusion of the substrate and whose colour was selectable via choice of dye and irradiating light wavelength.

Polymers should offer a potentially more versatile class of substrate material, capable of ultimate adaptation and use in organic media. Whereas polymers with inherent fluorescent groups do give electrofluorescent effects[2], they suffer from the need to use very high amplitude electric fields to achieve sufficient chain extension and alignment. This is true also for dye-tagged polymeric chains. There is a need for greater polymeric rigidity and, for a good switch, highly directional dye binding.

Poly(tetrafluoroethylene) (PTFE) can be emulsion polymerized in the form of stable, latex particles[3]. Standard procedures generally result in nearly spherical particles of some 0.2 μm diameter. In aqueous dispersion, they are highly birefringent when aligned in an external force field. So high is their inherent birefringence that they form standard media for the adjustment and calibration of electro-optic apparatus in this research group. The particles are therefore highly crystalline, indicating a high degree of order for the constituent polymer chains within the particles. Despite the extensive commercial utilization of the material, few studies of the structure and properties of the latex have been reported. The descriptive article by Rahl *et al.*[4] is noteworthy, however. These authors reported that, with certain preparations which had been prematurely terminated during the polymerization process, the near-spherical ellipsoidal particles were accompanied by the occasional flat, filamentous particle. From electron diffraction data, these authors suggested that the filaments were composed of polymer molecules essentially extended along the filament length and that these filaments are successively folded (*Figure 1*) to form the nearly spherical ellipsoidal particles mentioned above. Certainly this would account for the high crystallinity of these latex particles.

It occurred to us that the rigid PTFE particles might be candidates to which fluorescent dye molecules might bind and so provide a potential optical switch. This has proved to be the case, and preliminary data are presented herein.

THE METHOD

The principle used has been to mix solutions of a fluorescent dye with suspensions of emulsion polymerized PTFE and to allow the dye to physisorb onto the latex particles. The optical properties of the material so obtained have been investigated by measuring each of the

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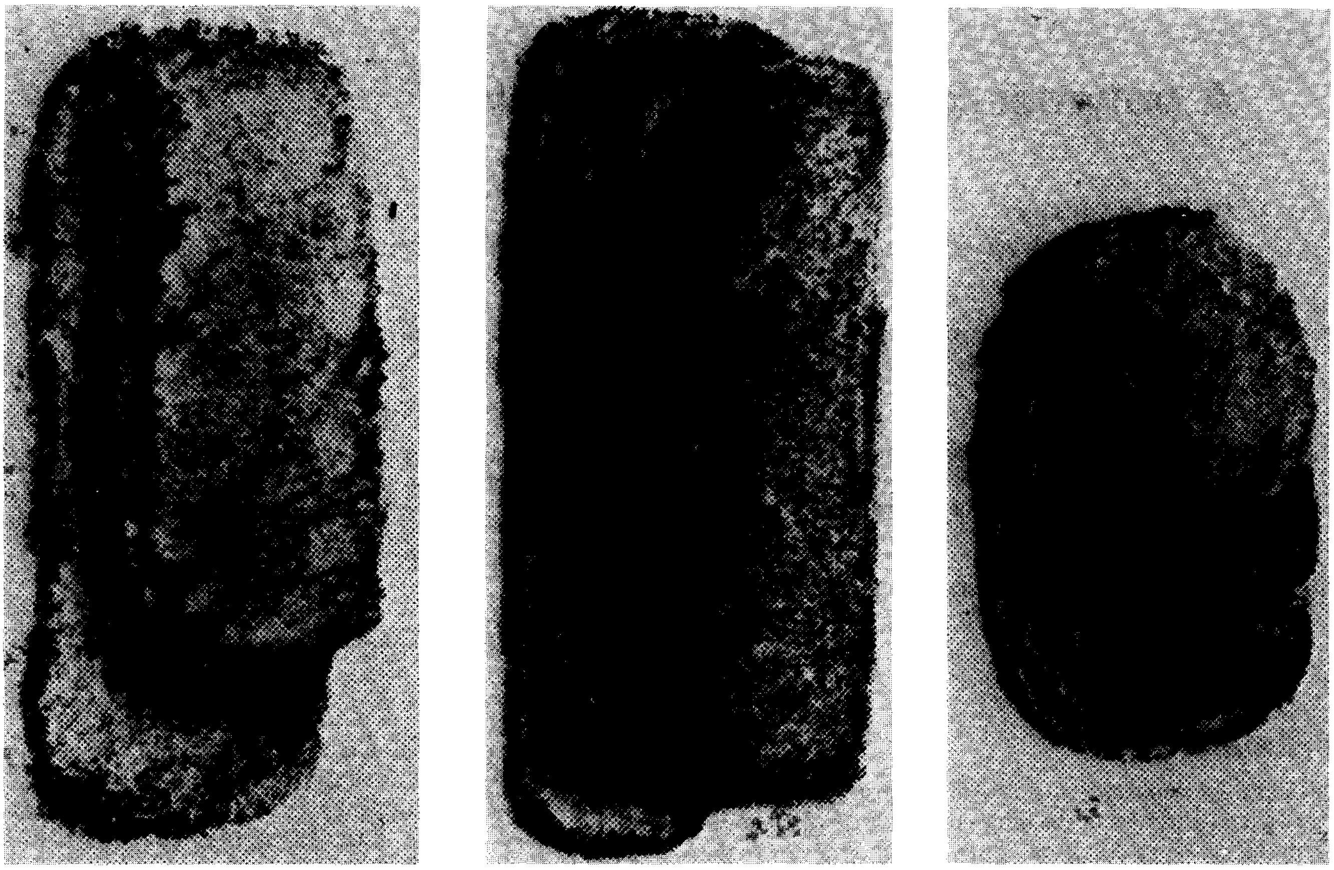

Figure 1 Model of PTFE lozenges: taken from ref. 4 by Rahl *et al.* (with permission)

four polarized components of the fluorescence V_v, V_h, H_v and H_h when vertically (capital V) or horizontally (capital H) polarized light was incident on the sample. Subscript symbols indicate the polarization state of emitted and detected fluorescent light. Any generalized component is indicated by F_f with F indicating V or H. Each of these components, and changes in them (ΔF_f) when the media were subjected to electric fields were recorded at 90° observation. Pulsed electric fields were then applied and the changing polarized components of the fluorescence monitored. The responses were transient in form (*Figure 3*) as the PTFE particles aligned against the randomizing influence of Brownian forces. Pulses were of sufficient duration to allow an equilibrium orientation to be achieved. Termination of a pulse was followed by a decay of the fluorescence change back to the pre-field value. Although not discussed here, the rates of establishment and decay can be used to indicate the particle sizes[5]. From measurements of the inherent depolarization of the fluorescence in the absence of the field ($\rho = V_h/V_v$) and the component changes ($\Delta F_f/F_f$), the switching contrast of the media could be assessed. For a full estimation of the properties, theory indicates that an estimate of the value of ($\Delta H'_h/H'_h$) is also required where the prime indicates data at the straight-through rather than the 90° observation direction.

It will be shown elsewhere that, if I_V be the total fluorescent output over all angles when vertically polarized light is incident on the sample and I_H be the corresponding intensity with horizontally polarized incident light, then

$$\frac{(I_V)_e}{(I_V)_o} = \frac{\left[1+\frac{\Delta V_v}{V_v}\right] + 2\rho\left[1+\frac{\Delta V_h}{V_h}\right]}{1+2\rho} \tag{1}$$

and

$$\frac{(I_H)_e}{(I_H)_o} = \frac{\left[1+\frac{\Delta H'_h}{H'_h}\right] + \rho\left\{\left[1+\frac{\Delta H_h}{H_h}\right]+\left[1+\frac{\Delta H_v}{H_v}\right]\right\}}{1+2\rho} \tag{2}$$

Here, subscripts e and o indicate the 'in-field' and 'pre-field' values. Obviously, in the absence of the field,

$$(I_H)_o = (I_V)_o = I_o \tag{3}$$

Both the individual component changes and the compounded intensity ratios expressed in equations (1) and (2) are used to assess the performance of the materials.

Two samples of PTFE were kindly supplied by Dr D. Rance of ICI, at 10% solids concentration in water. One sample consisted of a reasonable monodispersion of particles, of prolate ellipsoidal geometry, with a mean major dimension of approximately 200 nm and an axial ratio less than 1.5 as obtained from electron macroscopic data. Hence, the particles which were nearly spherical are referred to as 'lozenges'. The second sample was a suspension of these lozenges, but containing some 16% of rod-like particles (*Figure 2*). These were of the same breadth as the lozenges. They were of approximately 900 nm length and 6:1 axial ratio. This second sample is referred to as the 'fibrous-mixture'. Both suspensions had a dilute solution of the bi-benzimidazole dye Hoechst 33258 added to them. This dye fluoresces light green when excited by ultra-violet light. Free, unbound dye was washed out of the resulting suspensions, which were then diluted to final suspensions with 6 mg per 100 ml of polymer and some 10^{-3} times this weight of dye.

Light from an argon laser was suitably polarized in the vertical or horizontal direction and attenuated as desired using neutral density filters. The incident radiation was the mixed 351 and 364 nm spectral lines. It was directed at the relevant sample, which was held in a cylindrical cell between a pair of stainless steel electrodes mounted 2.5 mm apart. The emitted scattered and fluorescent light was collected by optical detection limbs at each of the two 90° directions in the incidence (horizontal) plane. Each optical limb consisted of filters to accept wavelengths in excess of 400 nm and to reject any incident scattered radiation. Polarizers ensured the acceptance of vertically polarized light by one detector and horizontally polarized light by the other. Photomultipliers transposed the remaining light intensity into an electronic signal which was then analysed, digitized and recorded.

RESULTS AND DISCUSSION

Electric fields of up to 2 kV cm^{-1} were applied in the form of short-duration pulses of 1.3 kHz alternating frequency and durations of 6 ms. The pulse method has three advantages. Firstly, practical devices often employ pulses for low current drain and to minimize heating effects. Secondly, the performance of the sample can be more rapidly assessed as in cases where a variety of dye-tagged samples have been studied. Thirdly, only the ratio of the relative *change* ($\Delta F_f/F_f$) in any polarized component of the fluorescence F_f is required in the analysis. This is readily obtained by recording the amplitude of the transient change in any fluorescent component compared with its pre-field value without the need to calibrate the intensities absolutely. Finally, the magnitude of any one component was field dependent, tending to a maximum value once the particles had fully aligned. This was achieved with fields of 2 kV cm^{-1} and only data for this condition are reproduced here.

Figure 2 Electron micrograph of the 'fibrous mixture' sample, consisting of both lozenge particles ($\simeq 0.2\,\mu$m diameter) and filamentous particles (length $\simeq 0.9\,\mu$m)

Figure 3 shows typical transient responses for one sample whilst *Table 1* gives the magnitude of the changes for both samples. Three other items were recorded. Firstly, the depolarization ratio differed slightly for the samples, but were of approximate value $\rho = 0.41(\pm 0.03)$. Secondly, the fluorescence of the dye was enhanced some 150% when bound to the latex compared with that in free solution. This is an obvious bonus for use in any fluorescence device. Thirdly, the switching or relaxation time was approximately 1 ms. This is faster than current commercial liquid crystal switches.

From the data, we note the following:

(i) The changes are significant. From the table an 80% change in V_v is achieved for the fibrous sample. The *total* fluorescence over all angles is 50% enhanced when vertically polarized light is incident, parallel to a vertical electric field direction.

(ii) Theoretical limits for a *complete* alignment of all fluorophores corresponds to limits of 3.0 and zero for the ratios $(I_V)_e/I_0$ and $(I_H)_e/I_0$, respectively.

(iii) Any device can operate by switching the applied field from a vertical to a horizontal direction with the

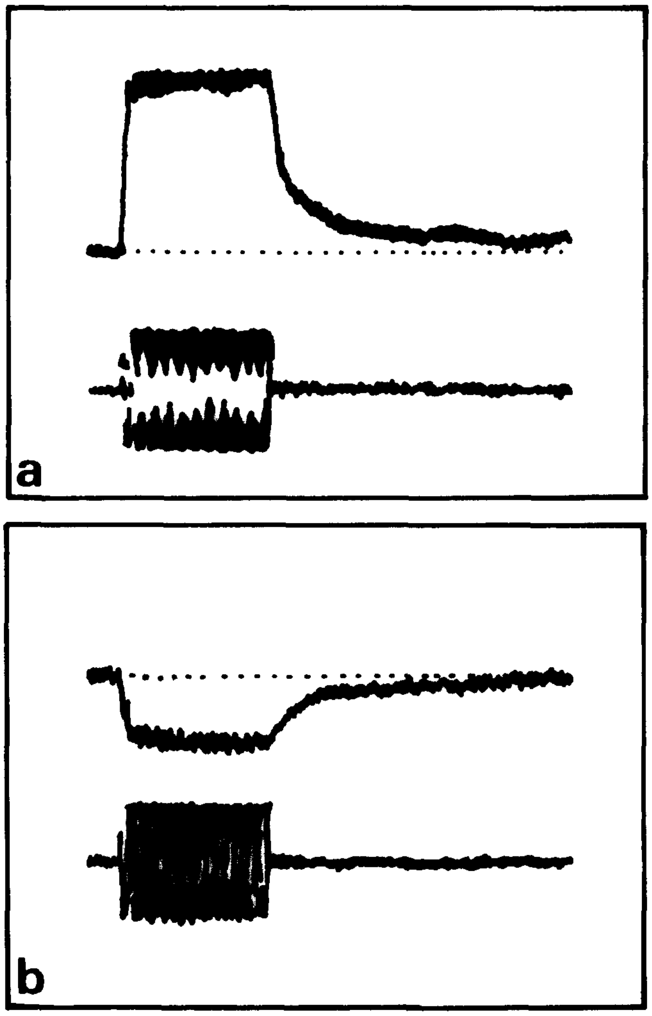

Figure 3 Changes in the polarized components of the fluorescence for the fibrous mixture. Frames (a) and (b) are for the V_v and H_h components, respectively. In each frame, the lower trace is the applied field of 2 kV cm^{-1} amplitude of 1.3 kHz alternating frequency and 6 ms duration. Time runs from left to right

Table 1 High-field induced changes in the polarized components of the fluorescence from suspensions of PTFE tagged with Hoechst 33258 dye

Sample	Relative changes ($\Delta F_f/F_f$) in components					Total intensity changes	
	V_v	V_h	H_v	H_h	H'_h	$\frac{(I_V)_e}{I_o}$	$\frac{(I_H)_e}{I_o}$
PTFE lozenges	+43%	+6%	−3%	+15%	−17%	1.26	0.87
Fibre and lozenge mixture	+80%	+16%	−6%	−25%	−34%	1.49	0.87

Data for $E=2\,\text{kV cm}^{-1}$

incident beam of fixed horizontal or vertical polarization. Alternatively, the field direction can be held in the vertical (or horizontal) plane and the polarization state of the incident beam switched from vertical to horizontal. In either case, the contrast between the last two columns of *Table 1* would be obtained.

(iv) The fibrous mixture sample gives twice the effect obtained with the pure lozenges. This indicates that 15% rod-like particles contributes an effect of the same order as 85% of lozenges.

The last mentioned is by far the most significant factor. An approximate estimate indicates that, if a suspension of 100% dye-tagged rod particles were available, it would give values of the order of

$$(I_V)_e/I_o=2.8 \quad \text{and} \quad (I_H)_e/I_o\simeq 0.11$$

These are extremely close to the optimal fluorescence limits, and indicate an extremely high anisotropic optical contrast switch. Attractions of the mechanism are:

(a) the high brightness of fluorescence;

(b) the availability of variable colours via the use of different dyes;

(c) the control of switching speed with the employment of PTFE substrates of selectable size.

A programme of studies is in progress to investigate a range of dye colours when bound to PTFE and other filament-forming polymers. The production of monodisperse, well-defined, small but rod-like polymer latex particles would be a welcome commercial development.

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