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Mechanochromic systems for the detection of stress, strain and deformation in polymeric materials

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The detection of stress in polymeric materials such as plastics, elastomers, composites and coatings is critical in the monitoring of material failure including stress fractures, fatigue and hysteresis. Mechanochromic systems that utilise a change in fluorescent output as a result of the mechanical deformation of a polymer have only been actively investigated relatively recently and whilst the field is still relatively small a considerable number of examples of such systems now exist. This article will discuss the principles behind such systems and review examples in the literature and survey the most common fluorophores used in such systems including phenylene vinylene oligomeric derivatives, polycyclic aromatic compounds, carbazole derivatives and conjugated polymers.

1. Introduction

The detection of stress in polymeric materials is critical in the monitoring of material failure including stress fractures, fatigue and hysteresis. It can increase the reliability of engineering materials such as plastics, composites, coatings and other polymeric materials. Methods used to detect internal stresses in elastomeric materials include photoelasticity,¹ laser Raman spectroscopy² and the bimetallic method³ but are usually

invasive or destructive and do not allow the analysis to be done for real-time *in situ* applications. Mechanoresponsive materials that convert mechanical events into a measurable output that can be monitored non-invasively at a distance from the material are ideal candidates for stress–strain measurements. In particular mechanochromic systems that utilise a change in fluorescent output with mechanical deformation have been actively investigated for around 15 years now and whilst the field is still relatively small a considerable number of examples of such systems now exist. This article will discuss the principles behind such systems and review examples in the literature.

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1.1 Mechanochromism and fluorescent spectroscopy

A mechanochromic approach holds considerable promise for a variety of applications such as the detection of residual stresses in moulded plastics, the prediction of mechanical failure by the prior detection of areas of stress and the direct measurement of stress during deformation. A mechanical input into the material is self-explanatory and includes deformation of the material under consideration such as tensile or compressive stress; for an *in situ* measurement of optical response to this mechanical deformation the most promising tool is the change in the optical response of groups or molecules within the materials. Fluorescent emission spectroscopy is possibly the most promising technique for monitoring polymeric material deformation and fluorescent spectroscopic techniques have been widely used to probe material properties in polymers, sol-gels and self-assembled aggregates in solution for example.^{5–7} The technique uses an environmentally sensitive fluorescent molecule termed a fluorophore (or fluorescent label) to measure the deformation induced stress in materials in a non-invasive and non-destructive way. The basic principles of fluorescent spectroscopy are well known. Simply put a fluorescent moiety absorbs UV-visible radiation exciting it from its electronic ground-state (S_0) to an electronic excited-state (e.g. S_1 or higher states) vibrational sub-level, giving $S_0 \rightarrow S_1$ electronic transition. The excited-state moiety quickly loses energy to non-radiative transitions e.g. collisions with surrounding molecules (vibrational relaxation) and steps down to the lowest vibrational sub-level of the excited state. The moiety then undergoes a radiative transition from the lower vibrational sub-level of the upper electronic state (S_1) to a vibrational sub-level in the electronic ground-state (S_0), losing the remaining excess energy as radiation (Fig. 1(a)). The emitted radiation spectral emission band is of a longer wavelength than that of the original excitation radiation, usually in the visible region and is termed fluorescent emission.^{8–10} These methods allow measurements to be carried out through the excitation and detection from the same surface of a material providing a way of analysing the material *in situ*. For example, other optical measurements, such as birefringence, optical dichroism, and UV-vis cannot be used to detect changes to the surface of materials since they require light to travel through the medium of the material. A number of fluorescent properties are amenable to measurement including steady-state measurement of changes in emission intensity, changes in time-resolved fluorescence such as decay times and changes in the fluorescent anisotropy.⁹ As will be seen measurement of changes in the excimer : monomer ratios with deformation are common, in part since such changes can result in distinct colour changes in fluorescent emission. Fluorophores can form complexes known as excimers, an excited-state dimer dissociated in its ground-state.^{11,12} The excimer complex is formed *via* the collisional interaction between an electronic excited-state fluorophore and another fluorophore in its electronic ground state, known as dynamic excimer formation. The excimer complex quickly dissociates back to the ground-state pyrene monomers emitting radiation of a longer wavelength than that of the excitation energy and is termed excimer fluorescence.^{13,14} An example of the emission spectrum for pyrene illustrating this phenomenon is given in Fig. 1(b). For more detail on all of these fluorescence techniques readers are directed to the text by Lakowicz.⁹

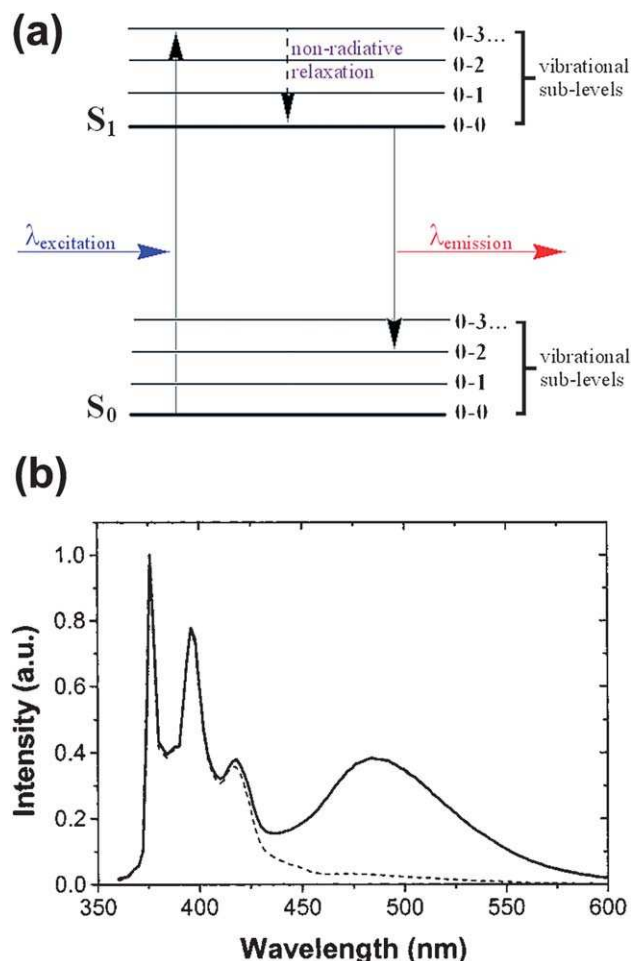


Fig. 1 (a) Simplified process of fluorescence excitation and emission. (b) Fluorescence emission spectra (λ_{ex} 342 nm) for pyrene-derivatives in toluene (... , $1 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^{-3}$ and —, $1 \times 10^{-1} \text{ mol}^{-1} \text{ dm}^{-3}$). Reproduced with permission from ref. 4.

1.2 Mechanical properties of polymers

The response of a polymeric material to external forces can vary largely depending on the materials characteristics and properties including chain length, chain entanglement, degrees of crystallinity and cross-linking, glass transition temperature and preparation of the materials. Application of an external force on a polymeric material will cause it to undergo a change in shape and upon release, the material can respond in several ways: (i) the material may not recover to its original dimensions and so has been permanently deformed; (ii) the material behaves elastically and recovers to its original dimensions and so can be followed by a form of Hook's law of elasticity¹⁵ which can be represented for a material as:¹⁶

$$F = -kx \quad (1)$$

Where F (in N) is the restoring force exerted by the material, k (Nm^{-1} or kg s^{-2}) is the force constant of the material *i.e.* stiffness and x (m) is the displacement of the material from its starting position (*i.e.* $x = 0$). However this law only applies for materials such as steel where the applied force (or stress) is

proportional to % extension (or strain) during elastic deformation. Materials such as polymers do not obey Hooke's law at high strains due to their complex responses to the applied forces. As such the applied force (stress) and the resultant extension (strain) are not linear as shown in Fig. 2.^{16–18} In the range where deformation is reversible and proportional to the stress, the tensile modulus, also termed Young's modulus (E), is used to measure the ratio of the tensile (or compressive) stress (σ , measured in MPa or N mm^{-2}) to the extension (or compression) strain (ϵ , measured in m):^{15,19}

$$E = \sigma/\epsilon \quad (2)$$

$$\sigma = F/A \quad (3)$$

$$\epsilon = l/l_0 \quad (4)$$

where F (MPa) = the force applied to the material, A (m) = the cross-sectional area, l_0 (m) = the length before extension and l (m) = the length after extension. Young's modulus can be determined experimentally from the slope of a stress–strain curve of an elastomeric material and gives a value of the resistance of a material to reversible longitudinal deformation.¹⁹

Fig. 2(a) displays representative stress–strain plots of some polymeric materials. The range of mechanical properties

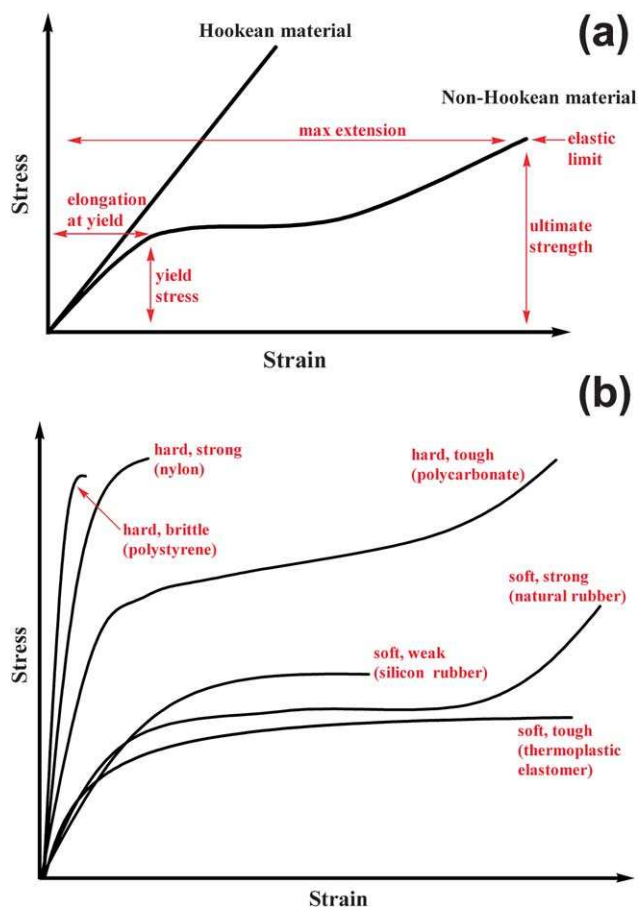


Fig. 2 Illustration of stress–strain plots for (a) typical Hookean and non-Hookean materials, and (b) various polymeric materials.

exhibited by polymeric materials ranges from tough brittle materials showing limited strain with applied stress, to rubbery materials with substantial strain with applied stress. Consequently the measurement of stress *via* an optical response to the mechanical deformation (strain) in the material needs to potentially cover an extremely large range (*e.g.* a change in response for elongation from 0.1 to 600%) or more feasibly, a variety of stimuli-responsive systems may be necessary according to the mechanical properties of the polymer.

The following review will discuss the systems utilised to date to obtain a change in fluorescent properties with stress/strain according to the general molecular structure of the fluorescent dye where possible. An equally valid approach would be the discussion of mechanochromic systems according to the nature of the polymeric material under study. This will be discussed in the summation and Conclusions.

2. Fluorophores for measurement of polymer deformation

2.1 Carbazole fluorophores

A reversible and nondestructive method in the optical analysis of internal tensile stress–strain in a PS polymer matrix was demonstrated by Ikawa *et al.*²⁰ Poly(*N*-vinylcarbazole) (PVCz) fluorophores (Fig. 3(a)) were dispersed non-covalently into a polystyrene (PS) matrix at a concentration of 0.05 wt%. Cast films were stretched to strain values of 0–0.8% and the fluorescent emission spectrum (Fig. 3(b)) showed a general decrease in monomer emission (340–360 nm) and an increase in the partial-overlap excimer emission (360–430 nm). The emission due to the full overlap excimer emission (430–500 nm) was found to be unchanged with the increase of strain and thought to be due to the restriction of the molecular motion of the PVCz chains by the rigid PS polymer matrix. The ratio of the fluorescent emission intensities (I_{375}/I_{345}) of the excimer (at 375 nm) to the monomer (at 345 nm) were proportional to the applied strain (Fig. 4(a)). The intensity ratio (I_{375}/I_{345}) was also used to study the stress–relaxation of the PVCz–PS films (Fig. 4(b)). The film was stretched to a strain value of 0.4% with an increase of the intensity ratio (from 1.15 to 1.23) and held whilst stress–relaxation occurred (from 15 to 10 MPa) during which the intensity ratio remained the same. Upon the removal of the applied strain, the intensity ratio was found to return to its initial value leading to the assumption that the intensity ratio is only affected by the strain and not by the stress.

Spanggaard *et al.* investigated the use of PVCz-polymers as stress-sensors in polystyrene–polyisoprene–polystyrene (SIS) elastomers, they proved too brittle to use and only gave strain values <1% beyond which they broke.²¹ Consequently they used carbazole units used as fluorescent labels to measure the strain caused by tensile elongation. The covalently labeled (~0.1 wt%) carbazole SIS derivatives (Fig. 5) were then cast into homogeneous transparent films which were uniaxially elongated up to 400% (Fig. 6(a)). The intensity of the 352 nm emission increased while the 370 nm emission decreased; thus the emission intensity ratio ($I_{352 \text{ nm}}/I_{375 \text{ nm}}$) increased with elongation values of 600% though the changes were most pronounced for strains from 0 to 200% (Fig. 6(b)). The ono-carbazole derivative (**1**, Fig. 5) gave

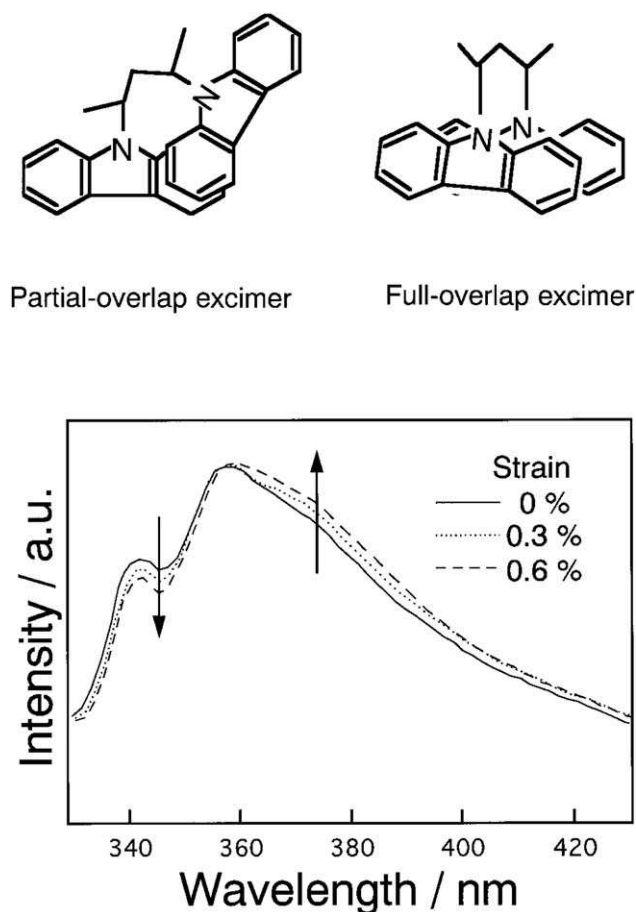


Fig. 3 (a) The partial and full overlap of the carbazole units in PVCz. (b) Steady state fluorescence spectrum of PVCz-PS film under stress (strain 0–0.8%). Reproduced with permission from ref. 20. © 1997 John Wiley and Sons.

similar responses to the biscarbazole derivatives (2–4, Fig. 5). Given that no excimer emission was evident the authors concluded that the intensity changes were due to changes in the intensities of the vibronic bands of the carbazole (monomer) units instead of the monomer/excimer balance (in contrast to the conclusions of Ikawa *et al.*) Thus while the labeling of SIS elastomers with carbazole fluorophores allowed measurements of strain at elongations up to 600% these were accompanied by significant degrees of error (Fig. 6) and the need for large sampling areas (>4–5 mm²) to average local variations of the sample surface.

2.2 Anthracene, naphthalene, perylene and pyrene fluorophores

Anthracene and derivatives. Amongst the earliest studies on fluorescence response with elongation of solid polymer samples were those of Jarry and Monnerie,²² Fajolle *et al.*²³ and Bur *et al.*²⁴ In all cases the changes in the fluorescence anisotropy with elongation were recorded. As part of a larger study of the effects of applied shear stress on polymer melts Bur *et al.* used anthracene-labeled polybutadiene (0.1 wt% anthracene) to study the change in anisotropy with extension.²⁴ They demonstrated a linear change in anisotropy values with extension (Fig. 7) which

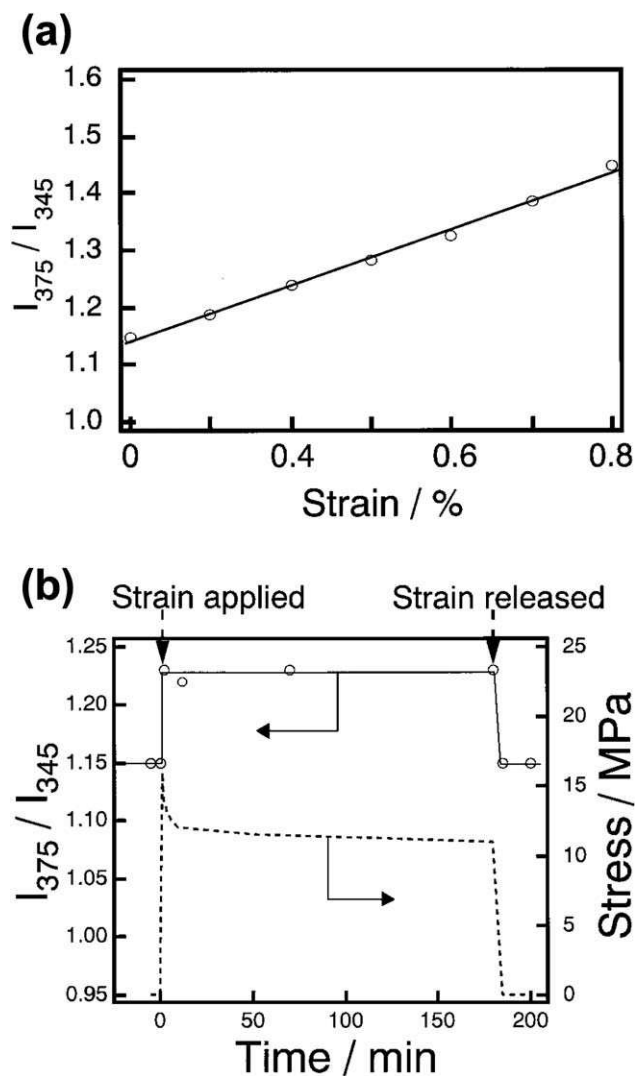


Fig. 4 I_{375}/I_{345} emission ratios versus (a) applied strain and (b) time compared with stress versus time. Reproduced with permission from ref. 20. © 1997 John Wiley and Sons.

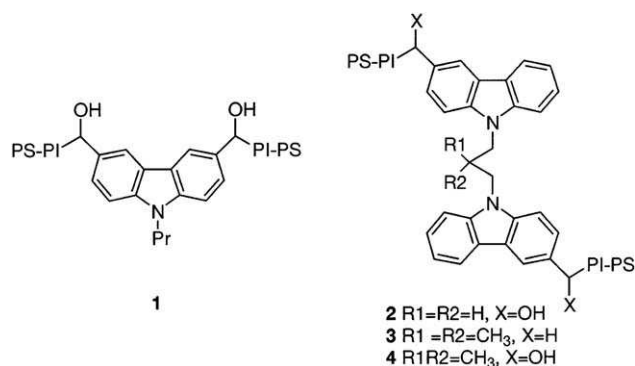


Fig. 5 Carbazole derivatives based on the carbazole unit used as fluorescent labels. Fluorophores are covalently linked to polyisoprene–polystyrene (PI–PS) elastomers. Reproduced with permission from ref. 21. © 2003 American Chemical Society.

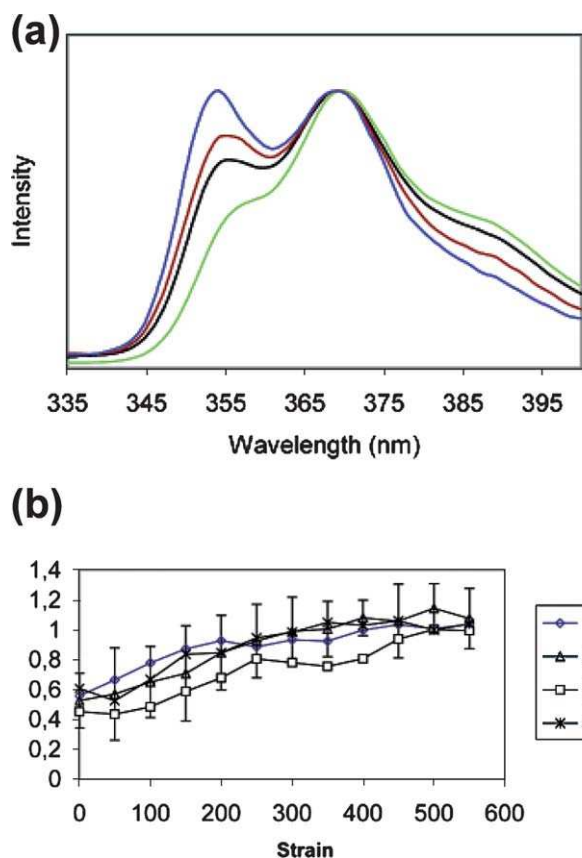


Fig. 6 (a) Representative emission spectra of carbazole labeled polyisoprene-polystyrene (PI-PS) at various elongations. (b) Emission intensity ratio (I_{352}/I_{375}) as a function of strain. Reproduced with permission from ref. 21. © 2003 American Chemical Society.

qualitatively agreed with the results of Monnerie *et al.* Shiga and Ikawa *et al.* demonstrated a change in the time resolved fluorescence of 9-methylanthracene (9-MeAn) in poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) containing carbon black.^{25,26} The decay time of coumarin 7, pyrene, 8-hydroxyquinoline, 9-bromoanthracene and 1,2-benzothio-*phene* fluorescence remained unchanged in uniaxially stretched

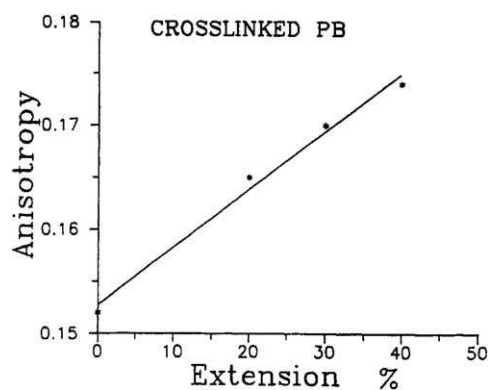


Fig. 7 Change in fluorescence anisotropy of anthracene labeled (0.1%) polybutadiene with elongation. Reproduced with permission from ref. 24. © 1992 American Chemical Society.

PMMA up to 10 MPa stress. In contrast 9-MeAn showed a decrease in lifetime of 0.5 s suitable for measurement of stress over the same range (Fig. 8(a)). Good agreement with residual stress measured by the bimetallic method was also noted for polymer films cured for 96 hours (Fig. 8(b)). 9-MeAn was also used to measure stress in PVC test pieces where a good correlation of lifetime with stress was observed for up to 3 MPa and 1.5% strain. Interestingly by applying strain and then releasing after an extended period they demonstrated that the major contributor to the change in lifetime could be ascribed to the stress rather than strain. Some basic surface mapping over the test piece of PVC was also demonstrated (Fig. 9).

Naphthalene derivatives. Yang *et al.* used copolymers of 1-naphthylmethyl methacrylate and methyl methacrylate (PNMMA) to study the orientational structure of poly(methyl methacrylate) PMMA.^{27,28} Films (thickness $\approx 30 \mu\text{m}$) were cast of the blends PMMA and PNMMA with 0.59 and 56 mol% 1-naphthyl content in PNMMA and 0.4 or 1 wt% PNMMA in PMMA. Samples containing low concentrations of the 1-naphthyl were found to have monomer dominated emissions (λ 340 nm) whereas higher concentrations had excimer dominated emission ($\lambda \approx 400\text{nm}$) due to increased intramolecular interactions in the polymer chains. Dumbbell shaped samples of the films were elongated to elongation ratios of 90% at 80 °C, whereupon it was

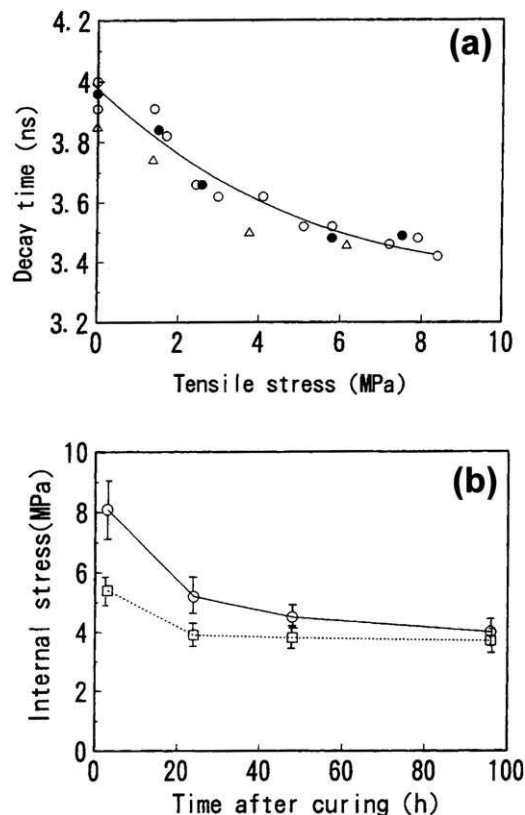


Fig. 8 (a) Change in decay time with tensile stress for 9-MeAn in uniaxial stretched PMMA film. (b) Comparison of internal stress in PMMA film determined by time-resolved fluorescence (circles) and the bimetallic method (squares). Reproduced with permission from ref. 25. © 1998 John Wiley and Sons.

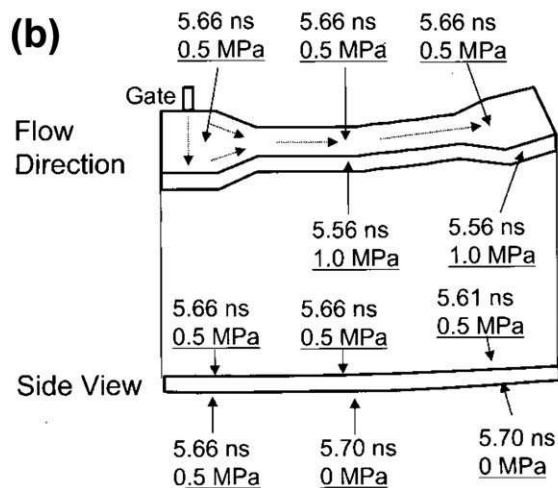
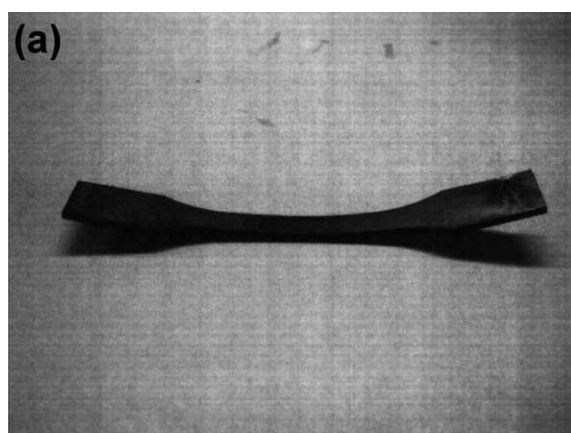


Fig. 9 (a) Dumbbell shaped piece of PVC with 9-MeAn dye and (b) the corresponding surface stress map determined from fluorescence lifetimes. Reproduced with permission from ref. 26. © 2002 John Wiley and Sons.

found that the excimer emission broadened with a larger λ_{\max} shifting to longer wavelengths (to 425 nm) due to multiple naphthyl ring interactions of the coiled polymer chains. However the increases in the intensity ratio were very small for such large elongation ratios (up to 80%) indicating that the system is not very sensitive to deformation.

Aznar *et al.* used a series of fluorophores (Fig. 10) incorporated into thermoset (two-part) epoxy films to measure the internal stresses upon film deformation, non-destructively and *in situ*.²⁹ The fluorophores (before curing of the epoxy film) were either (i) covalently labeled (*e.g.* DANPAS) or (ii) mechanically mixed into the epoxy polymer matrix. The mechanical properties of the epoxy films were found to be unaffected when incorporating low fluorophore concentrations *e.g.* $<10^{-3}$ M. Film samples were then elongated within their elastic region (*i.e.* non-destructively) using an optical cable to excite (λ_{ex} 310–365 nm) and record their fluorescent emissions (λ_{em} 320–650 nm), perpendicular from the sample surface (*i.e.* *in situ*). It was generally found that the fluorescent emission (integrated, with respect to relaxed state) intensities of both the covalently labeled and mechanically mixed fluorophores displayed a linear variation of intensity at low elongation (strain) values but leveled off at higher values (Fig. 10) The labeled elastomer displayed the

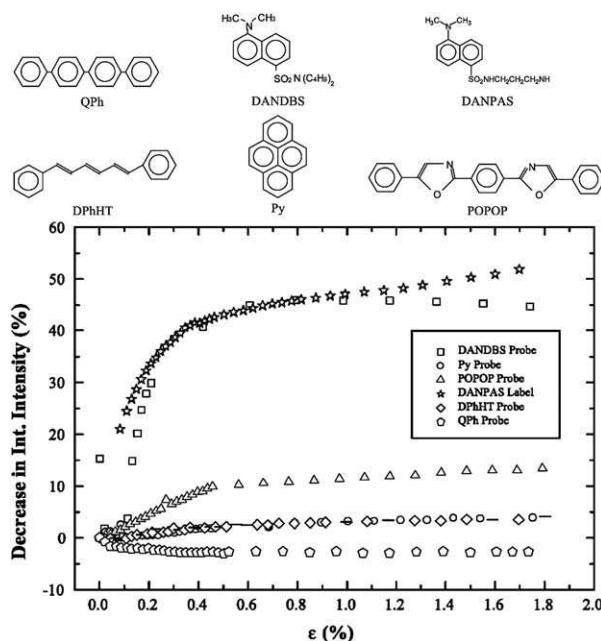


Fig. 10 Top, fluorophores studied as strain sensors in epoxy films and bottom, plot of integrated emission intensity as a function of strain for elongated film samples. Reproduced with permission from ref. 29. © 2003 Elsevier.

largest change in intensity at low strain values however the mechanically mixed probe (POPOP, Fig. 10) actually displayed higher sensitivity at higher strain values. The elastomers were also relaxed back to their initial states with the emission intensities generally decreasing back to their initial intensities, showing that the system is indeed reversible.

The authors postulated that the direct measurement of the emission light from the film samples depended on the sample thickness and fluorophore concentration and so may not be the optimal method for the analysis of stress in materials. The technique of measuring the first momentum of fluorescence $\langle \nu \rangle$ of the fluorophores in the film sample was then used. This method relies on the fact that material stress may increase the viscosity and/or rigidity of that material causing a blue-shift in the incorporated fluorophores fluorescence band, and can be represented as:

$$\langle \nu \rangle = \int \nu I(\nu) / \int I(\nu) \quad (5)$$

Where ν = the wavenumber of the emission band and I = the intensity of emission. It was found that the fluorophore DPhHT displayed the largest change in $\langle \nu \rangle$ with the other fluorophores displaying small to insignificant changes using this analysis method (Fig. 11(a)). Furthermore, a film sample containing the DPhHT with a purposely made hole (diameter 5mm) was uniaxially stressed and variation in $\langle \nu \rangle$ in 2D (Fig. 11(b)) indicated an accumulation of stresses along the load axis and around the hole in the film sample. In conclusion, the incorporation of fluorophores into epoxy films either *via* covalent labeling or mechanical mixing, the system could demonstrate a reversible, nondestructive and *in situ* method in the optical analysis of stress.

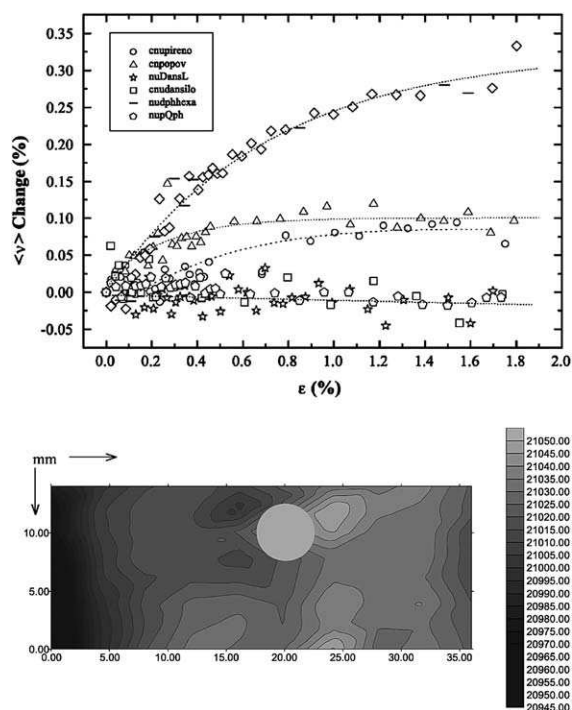


Fig. 11 Top, plot of the first momentum $\langle \nu \rangle$ of emission as a function of strain for various fluorophores in elongated epoxy film samples. Bottom, fluorescent mapping of an elongated film sample (DPhHT fluorophore) with mechanical damage (a hole) using the first momentum $\langle \nu \rangle$. Reproduced with permission from ref. 29. © 2003 Elsevier.

Perylene and derivatives. Pucci *et al.* used perylene³⁰ and perylene-3,4,9,10-tetracarboxyldiimide (PTCDI) derivatives³¹ dispersed into LLDPE films to study their optical and mechanical (stress–strain) properties. The perylene and PTCDI derivatives (Fig. 12) were typically dispersed into LLDPE films *via* melt processing techniques at concentrations of 0.01 wt% to 0.1 wt%

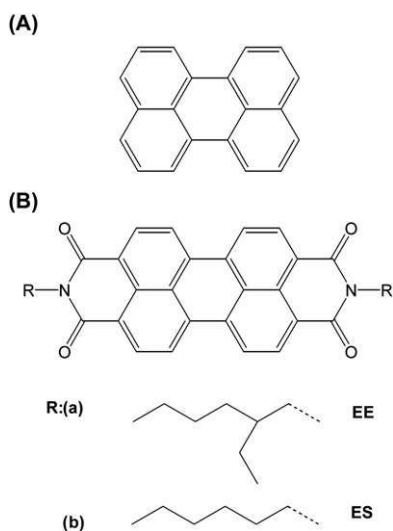


Fig. 12 a) Perylene and (b) PTCDI derivatives; EE-PTCDI and ES-PTCDI, fluorophores utilised in dichroic studies of doped PE films. Reproduced with permission from ref. 31. © 2003 American Chemical Society.

for PTCDIs and 1 wt% to 2 wt% for perylene. The perylene and PTCDI dye molecules dispersed into LLDPE at low concentrations displayed monomer emissions (colours; blue for perylene and yellow for PTCDIs) and at high concentrations displayed excimer emissions (colours; yellow for perylene and red for PTCDI). The films were mechanically elongated (to draw ratios 0–8) either at ambient or high temperatures (90 °C). It was typically found for the perylene and PTCDIs film samples (containing high concentrations of dye molecules) displayed colour changes from excimer dominated emissions to monomer dominated emissions (*e.g.* Fig. 13) due the break-up of the perylene and PTCDI dye aggregates. The isolated dye aggregates or molecules dispersed into the amorphous phase were also underwent uniaxial alignment along the stretching direction as a consequence of the disruption of the dye aggregates. Consequently these films displayed high dichroic behaviour as evidenced by observations with polarised light parallel and perpendicular to the drawing direction. No direct correlation of change in colour/emission properties was made with stress or strain in these cases.

Pyrene. Recently Holder *et al.* incorporated and pyrene-derivatised PDMS samples and a triethoxysilyl-pyrene derivative in the Sn catalysed cure of a tetraethoxysilane α,ω -dihydroxyPDMS mixture giving pyrene labelled PDMS elastomers (Fig. 14(a)).³²

Studies with DSC and DMA suggested little change in the thermal and mechanical properties of the elastomer with pyrene incorporation. Fluorescence spectroscopy showed both monomer and excimer emission peaks in all samples. Uniaxial extension of the Py-TEOS labelled elastomer resulted in an increase in both monomer and excimer emission peaks (Fig. 14(b) and (c)) and a drop in the $I_E : I_M$ ratio with strain (Fig. 14(d)). Elongation (~ 0 to 20%) followed by relaxation showed no hysteresis for the fluorescent response and the results were reproducible over repeated cycles of extension and relaxation.

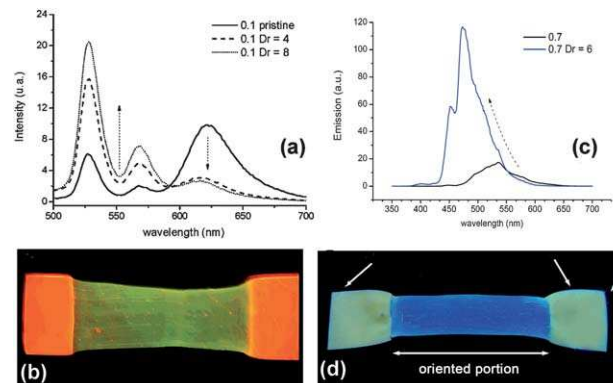


Fig. 13 (a) Change in emission intensity with draw ratio for (a) EE-PTCDI/LLDPE and (c) perylene/LLDPE. (b) Optical image (λ_{ex} 366 nm) of uniaxially oriented film EE-PTCDI/LLDPE (0.1 wt% EE-PTCDI). (d) Optical image (λ_{ex} 366 nm) of uniaxially oriented film perylene/LLDPE (0.7 wt% perylene). Arrows (top) indicate shearing stress caused during film preparation. Reproduced with permission from ref. 30 and 31. © 2003 American Chemical Society.

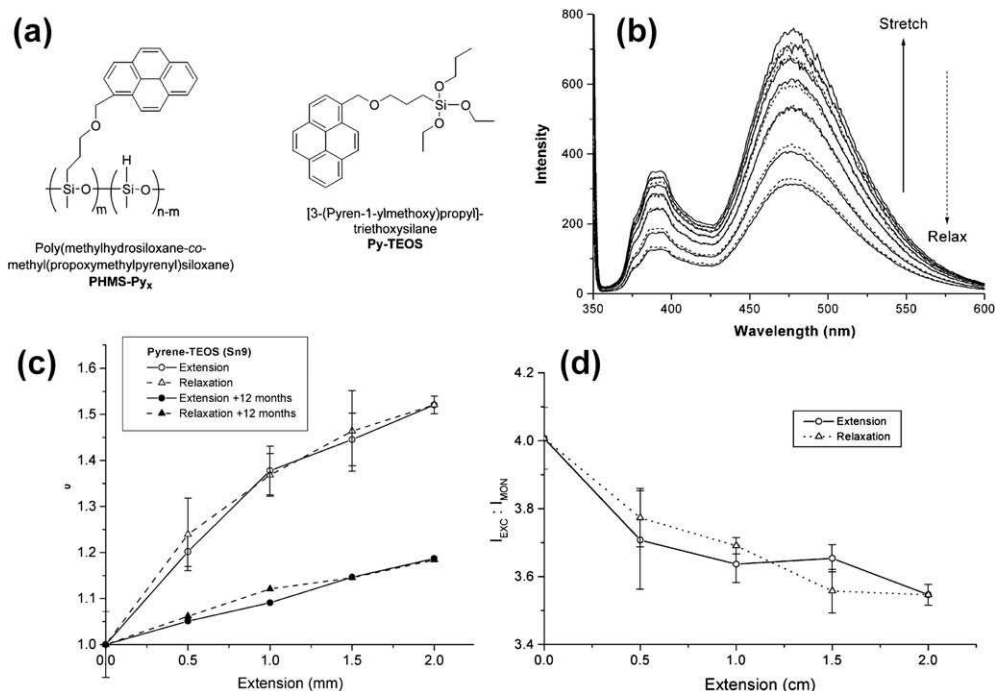


Fig. 14 (a) Structures of pyrene derivatives used in strain sensing of polydimethylsiloxane elastomers. (b) Change in emission spectra with uniaxial elongation of Py-TEOS labelled PDMS elastomer. (c) Plot of excimer emission intensity with extension. (d) Change in excimer : monomer emission intensity ratios with elongation. Reproduced with permission from ref. 32. © 2009 Royal Society of Chemistry.

2.3 Extended π -conjugated molecules

Poly(3-alkylthiophenes). The earliest instance of utilising a fluorescent extended π -conjugated system in stress-strain analysis was demonstrated by Ikawa *et al.* they used poly(3-alkylthiophenes) with butyl-, hexyl- octyl- and dodecyl-chains dispersed in PMMA.^{33,34} Up to 2% strain the steady-state fluorescence spectra of the samples remained unchanged however the time-resolved fluorescence was observed to change over this range. The decay time of fluorescence decreased significantly over the elastic deformation range of PMMA (0–0.2% strain) (Fig. 15(a)). Over the plastic strain range of PMMA (up to 100%) the steady-state fluorescence showed significant changes with a red-shift of the fluorescent maximum and a decrease in fluorescence intensity with strain (Fig. 13(b)). Decay times were observed to increase with strain over the plastic deformation range though the change was relatively small (~5% changes) and no correlation of stress with decay time was observed. The importance of the interaction of the PAT with the PMMA matrix was determined by the strongest changes occurring for the PAT with the longest alkyl chain (dodecyl-) and the highest molecular weight.

***p*-Phenylene vinylene derivatives.** Perhaps the most extensive studies of stress-responsive polymer systems with the most visually dramatic results have been carried out by the group of Weder. They utilised a number of extended π -conjugated dye molecules in a variety of polymeric materials. Cyano-oligo(*p*-phenylene vinylene) (cyano-OPV)³⁵ derivatives (structures 1–3, Fig. 16(a)) were dispersed into a copolymer of linear low density polyethylene (LLDPE) and octane (C8) comonomer, to study the

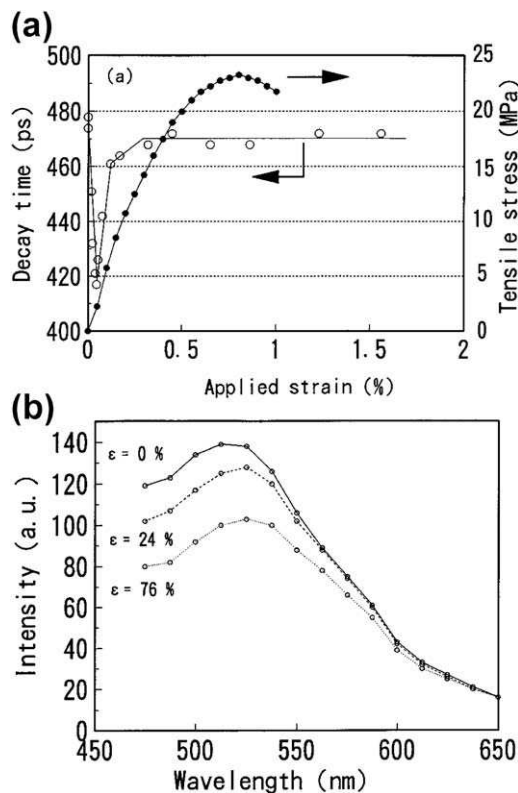


Fig. 15 Change in (a) fluorescence decay times and (b) emission spectra of poly(3-octylthiophene) in PMMA with strain. Reproduced with permission from ref. 34. © 1998 John Wiley and Sons.

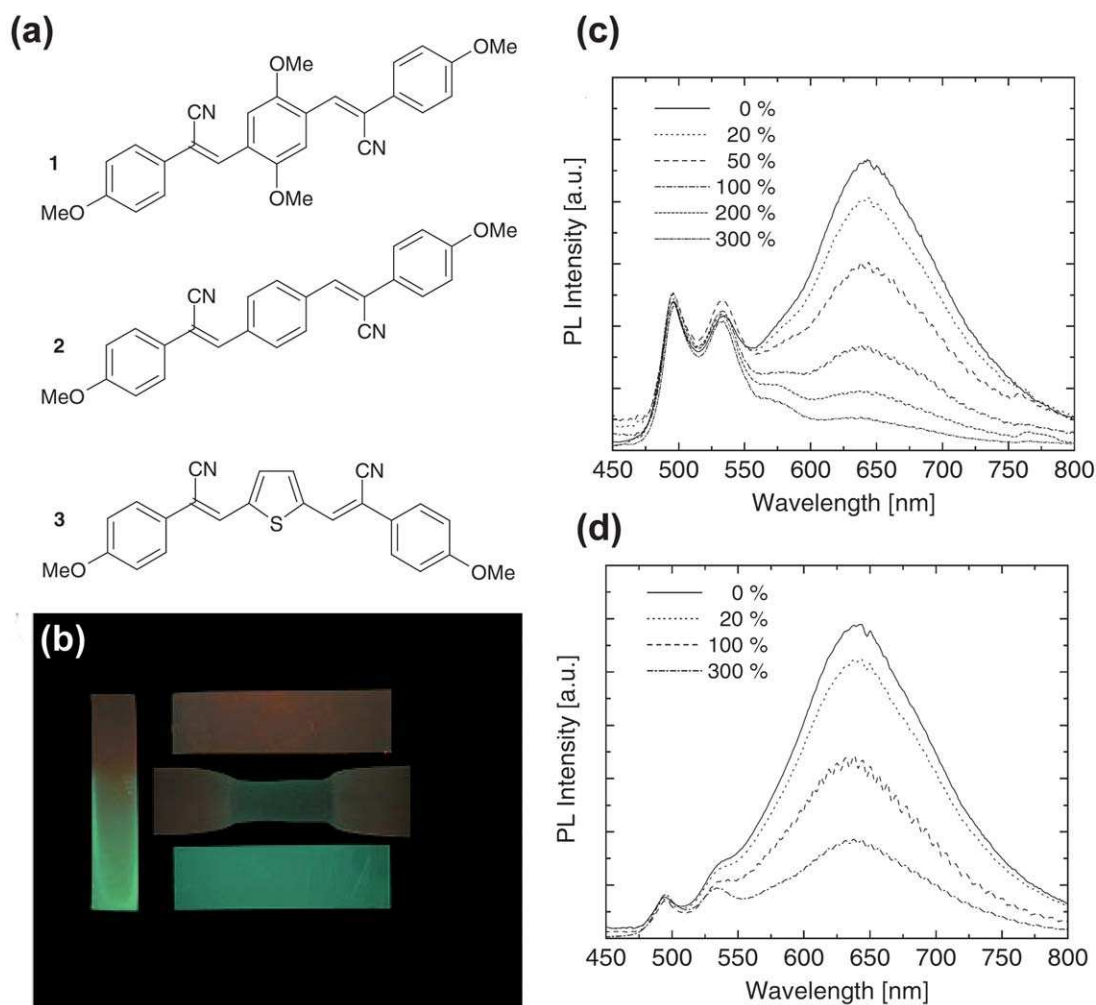


Fig. 16 (a) Cyano-OPV derivatives (structures 1–3) and (b) optical micrographs (λ_{ex} 365 nm) of film samples (cyano-OPV derivative, structure 1); unstretched films (top and bottom) stretched film (centre) and film exposed to high temperatures. Green colour (monomer emission) and red colour (excimer emission). Fluorescent emission spectra of film sample as a function of draw ratio in tensile orientated films (containing cyano-OPV derivative, structure 1) (a) LLDPE-1.2-C8 and (b) LLDPE-9.3-C8. Reproduced with permission from reference ref. 35. © 2002 Wiley-VCH Verlag GmbH & Co. KGaA.

deformation-induced colour changes upon tensile deformation (Fig. 16(b)). For example the cyano-OPV derivative (structure 1) was dispersed into LLDPE-C8 copolymer film samples LLDPE-1.2-C8 (1.2% C8) and LLDPE-9.3-C8 (9.3% C8) *via* guest diffusion. Guest diffusion involved the swelling of the film samples with solutions (dichloromethane or toluene) of the cyano-OPV derivatives with controlled dyeing parameters: concentration (1–20 mg mL⁻¹), temperature (25–70 °C) and time (~5 to 18 h). It was generally found that film samples dyed for short times, with low concentrations and at low temperatures displayed green monomer fluorescence emissions (λ_{em} 461 nm to 538 nm) (Fig. 16(b)). Upon increasing the dyeing parameters it was found that the films displayed red excimer fluorescence emissions (λ_{em} 550 nm to 644 nm) (Fig. 13(b)) due to aggregation of the dye (cyano-OPV derivatives) molecules. The homogenous film samples were then elongated to draw ratios of up to 400%. It was generally found that the intensity of excimer fluorescence emission in the films samples decreased with increased elongation draw ratios (Fig. 13(c) and (d)). For example it was found that

for the film sample LLDPE-1.2-C8 (LLDPE with 1.2 wt% C8) the decrease in excimer fluorescence with increasing elongation produced a colour change (at draw ratios 200–300%) from red to green. This was thought to be due to the phase-separation of the dye aggregates (excimer) into a molecular dispersion (monomers). This was also found to be in contrast to the film sample (LLDPE-9.3-C8) which did not show a colour change upon film elongation due to excimer emission still dominating (Fig. 13(d)). Further studies also found that the excimer fluorescence emission was also temperature dependent *i.e.* thermally stimulated. For example it was found that at temperatures >65 °C the phase separation of the dye aggregates occurs relatively fast (minutes) compared to temperatures <65 °C (hours). This was thought to be due to the temperature sensitivity of the dye molecules within the melting range of the host polymer. In conclusion, the films generally display reproducible colour change upon film deformation due to the phase separation of the dye aggregates in to molecular dispersions. However, the films have to be irreversibly elastically deformed to achieve this. The cyano-OPV derivatives

(structures **1**, **2** and Fig. 16(a) and BCEDB, Fig. 17(a)) were also dispersed into LLDPE films *via* melt-processing techniques.³⁶ The derivatives were mechanically mixed into LLDPE (concentrations 0.01–0.8 wt%) at high temperatures (180 °C), compression-molded into films and then rapidly quenched (to prevent large-scale phase separation between the dye molecule and the polymer host). Low concentrations of the cyano-OPV derivatives in the LLDPE films generally displayed monomer fluorescence emission (448 nm to 540 nm) and higher concentrations (>0.02 wt%) of generally displayed excimer fluorescence emission (573 nm to 644 nm). It was also found that the excimer emission intensity actually increased over time (0 to 3 months) and was thought to be due to the quenching of the films kinetically trapping the dye molecules in a molecular dispersion (monomers), even at high dye molecule concentrations (Fig. 17). The films containing the dye molecules were thermodynamically unstable at ambient conditions causing the slow aggregation of the molecularly dispersed dye molecules and hence an increase in excimer emission intensity. In order to speed up the aggregation of the dye molecules, the film samples were swelled in solutions of hexane (15 minutes) resulting in instantaneous aggregation. The tensile elongations of the films displayed deformation-induced colour changes with increased elongation ratios (from 0% to 500%) with I_M/I_E ratios increasing up to a factor of 10. For example it was found that for the film sample (0.20%wt, structure **2**, Fig. 16) a decrease in excimer fluorescence with increasing elongation produced a colour change from green (excimer emission) to blue (monomer emissions) (Fig. 17(b)). More recently a detailed study of the incorporation of these OPV derivatives in PE has been described.³⁷

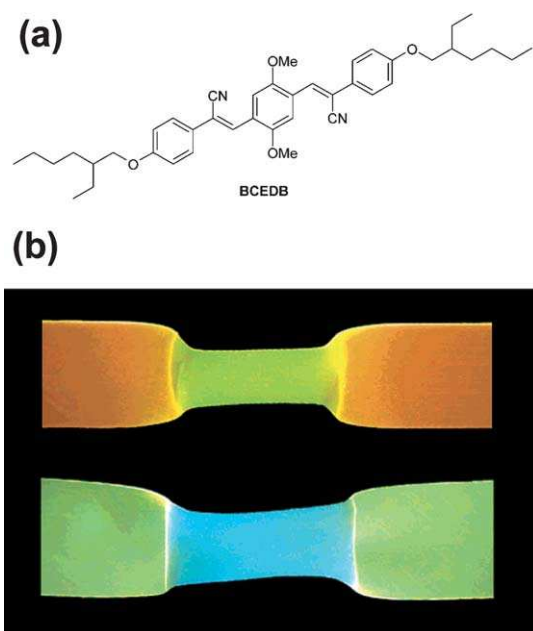


Fig. 17 (a) Structure of BCEDB and (b) optical micrographs (λ_{ex} 365 nm) of film samples: top (0.18%wt structure **1**, Fig. 16); green colour (monomer emission) and red colour (excimer emission) and bottom (0.20%wt, structure **1**, Fig. 16); blue colour (monomer emission) and green colour (excimer emission). Reproduced with permission from ref. 36. © 2003 American Chemical Society.

The general versatility of this approach to stress sensing was illustrated by the utilisation of the OPV derivatives in a variety of polymers. Weder *et al.*^{38,39,40} used OPV-derivatives incorporated into PMMA or poly(bisphenol A carbonate) (PC) polymers and also into poly(ethylene terephthalate) (PET) or poly(ethylene terephthalate glycol) (PETG) *via* melt-processing techniques, for use as threshold temperature and deformation sensors. In all examples as well as those already discussed (*vide supra*) the OPV-derivatives were found to be temperature dependent and thermodynamically unstable due to the methods of incorporating them into the polymer matrix or due to the low T_g of the host polymer. On the other hand, tensile deformation of the films was reproducible indicating a high degree of emission intensity changes from monomer dominated emission to excimer dominated emissions. This was found to result in dramatic colour changes, although the films have to be irreversibly elastically deformed to achieve this. As noted by the decrease in excimer emission with increasing elongation ratio showed an opposite effect to results obtained by Yang *et al.*⁴¹ where excimer fluorescence was found to increase with elongation (*vide supra*). The system studied by Yang *et al.* involved the physical labelling of the naphthalene fluorophore directly onto the polymer chain backbone. The elongation of the polymer host matrix forces the orientation of the polymer chain segments and side groups along the film drawing direction and hence leads to the increase of excimer forming sites and excimer fluorescence. In the system studied by Löwe and Weder the cyano-OPV fluorophores are not covalently bonded to the polymer backbone but are physically (non-covalently) dispersed into the polymer matrix. Upon elongation of the films (*i.e.* films containing high concentrations of the dye molecules) the dye aggregates are physically separated from each other by the polymer matrix into a molecular dispersion. This is reflected in the large decrease in excimer emission intensity and in fact it can be seen in Fig. 16(c) that there is a slight increase in the monomer emission intensity due to the increase in the molecular dispersion *i.e.* increase in monomer formation. When the OPV derivatives were added to polyurethanes *via* melt-processing (0.05–0.4%) the resulting systems displayed only modest changes in fluorescent response to deformation.⁴² However covalent incorporation of an OPV derivative into a polyurethane (Fig. 18(a)) led to significant changes in PL colour change with stress (Fig. 18(b)). The stress–strain curves for these systems were closely mirrored by the $I_E : I_M$ plots *versus* strain (Fig. 18(c)) showing the excellent potential of these systems as intrinsic stress–strain sensors. The covalent incorporation of OPV dyes has also been demonstrated for PETG films⁴³ and most recently the dispersions of OPV dyes in poly(vinylidene fluoride) has been reported.⁴⁴ In the latter case good correlation between I_M/I_E ratios with strain and stress–strain curves was obtained and furthermore the critical nature of the aggregation state of the dye in the mechanochromic performance was highlighted and noted as different from the cases involving PE films.

Poly(*m*-phenylene ethynylene)-*alt*-(*p*-phenylene ethynylene)]. Pucci *et al.*⁴⁵ used a fluorescent cyano-containing poly[*(m*-phenylene ethynylene)-*alt*-(*p*-phenylene ethynylene)] derivative (CN-PPE) dispersed into LLDPE to study dichroic behaviour caused by anisotropic orientation under tensile elongation.

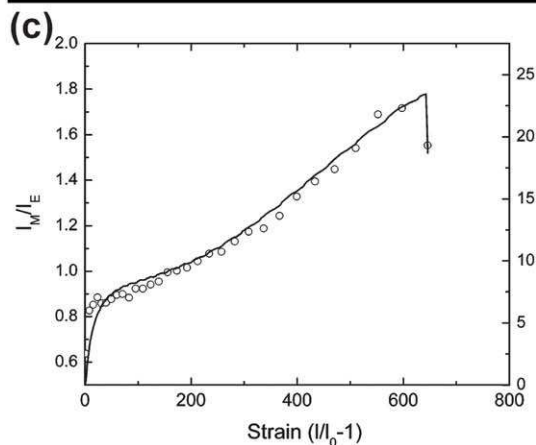
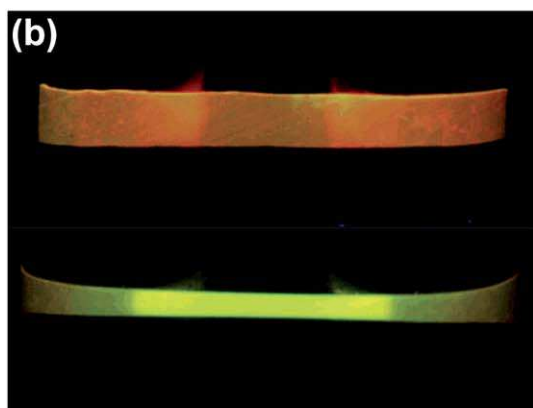
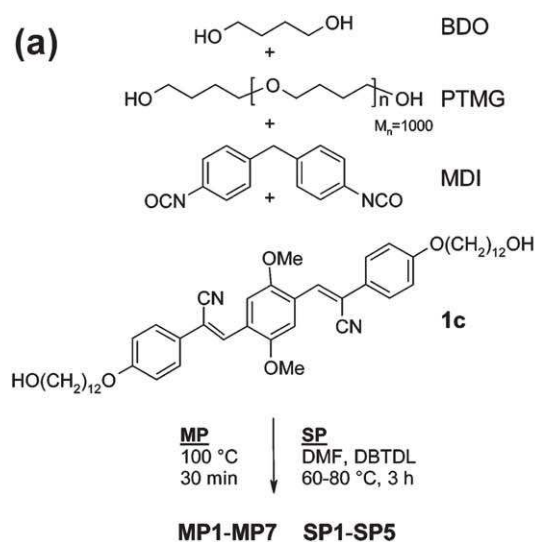
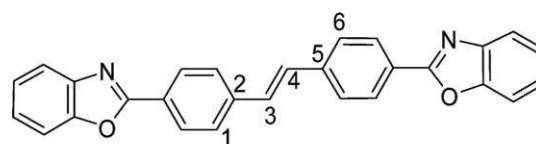


Fig. 18 (a) Synthesis of fluorescently labelled thermoplastic urethanes (TPUs MP1–MP7 and SP1–SP5). (b) Pictures (taken under excitation with UV light of a wavelength of 365 nm) of a film of MP6 in top, unstretched and bottom stretched state. (c) Ratio of monomer to excimer emission, I_M/I_E (circles, measured at 540 and 650 nm), and tensile stress (solid line) as a function of strain for films of SP4. Reproduced with permission from ref. 42. © 2006 American Chemical Society.

CN-PPE was dispersed in to LLDPE (0.02 wt% to 0.3 wt%) *via* melt processing techniques producing CN-PPE/LLDPE films. Films with low concentrations of CN-PPE (<0.1 wt%) displayed a blue monomer emission (~450 nm) and with higher

concentrations (>0.1 wt%) a green excimer emission (~480 nm). This was due to intermolecular or interchain fluorophore interactions caused by the planar conformation of the (CN-PPE) polymer chains in the solid (film) state *i.e.* aggregation of the CN-PPE fluorophores. The film samples were then elongated to draw ratios (of 10) at high temperatures (100 °C) with their fluorescence emission recorded using polariser's. The elongated CN-PPE/LLDPE film (0.2 wt% CN-PPE) displayed dichroic behaviour with green (excimer emission) to blue (monomer emission) visible dependent on the polariser viewing angle (0° parallel and to 90° perpendicular). This was thought to be due to the orientation of the CN-PPE fluorophore molecules caused by the orientation of the host (LLDPE) polymer matrix in which the long range fluorophore interactions are very anisotropic. However, no significant change in emission properties due to tensile elongation was observed. This was postulated to be due to the resistance of the CN-PPE aggregates to polymer host deformation contrasting with the results obtained by Weder *et al.* for the small molecule OPV derivatives in LLDPE films.

Stilbene derivatives. A series of further studies by Pucci *et al.* used fluorescent bis(benzoxazolyl)stilbene (BBS) (Fig. 19) dispersed into poly(propylene) (PP),⁴⁶ LLDPE,⁴⁷ poly(1,4-butylene succinate) (PBS)⁴⁸ and other polyolefins⁴⁹ to study their dichroic, anisotropic and thermal stimulation characteristics. BBS was dispersed into the various polymer films (thickness 80 μm to 200 μm) *via* melt processing techniques (*e.g.* 0.02 wt% to 0.5 wt%). It was typically found that at low concentration of BBS (<0.02 wt%) the films displayed blue monomer emission and higher concentrations (>0.02 wt%) displayed green excimer emission. The BBS aggregates (excimers) were also found to be thermally stimulated at high temperatures (*e.g.* 130 °C in PP films) displaying a collapse of the excimer emission band and producing a reversible colour change from green (excimer emission) to blue (monomer emission) in the order of minutes. The film samples were uniaxially stretched at high temperatures (*e.g.* 100 °C to 130 °C) for example for the film sample PP/BBS (0.5 wt % BBS), with the orientated parts of the films displaying emission colour changes from green (excimer) to blue (monomer) as shown in Fig. 20(a) and (b). This was thought to be due to the break-up of the molecular BBS aggregates (excimers) as a consequence of PP host matrix orientation due to tensile film elongation, favouring the uniaxial orientation of BBS monomers. In general it was thought that the degree of dispersion of



4,4'-Bis(2-benzoxazolyl)-stilbene
(BBS)

Fig. 19 Structure of bis(benzoxazolyl)stilbene (BBS) used as a stress responsive fluorophore in poly(propylene) (PP), LLDPE and poly(1,4-butylene succinate) (PBS). Reproduced with permission from ref. 47. © 2006 American Chemical Society.

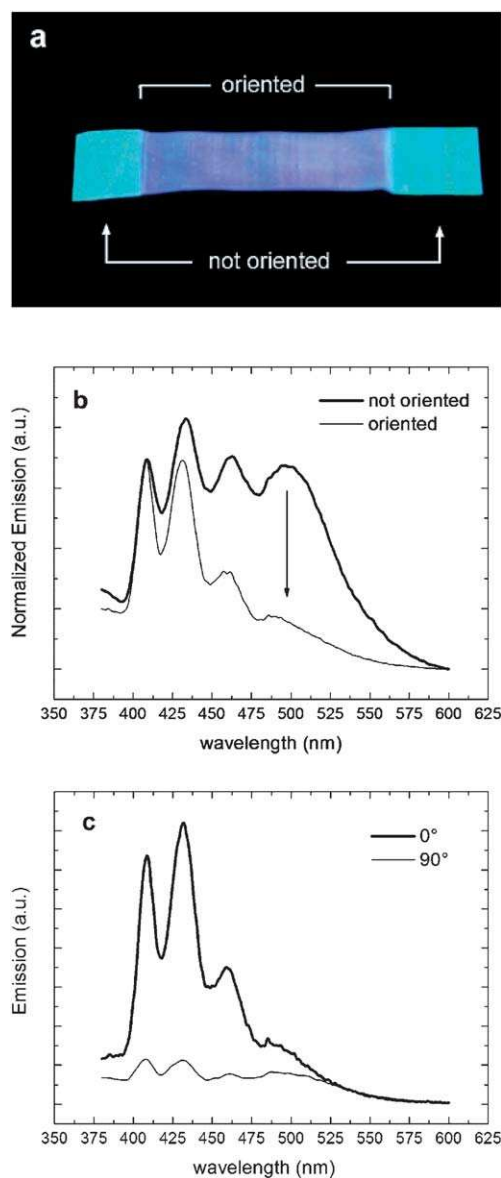


Fig. 20 (a) Optical image (λ_{ex} 366 nm) of uniaxially oriented film PP/BBS (0.5 wt% BBS). (b) Fluorescence emission spectra (λ_{ex} 277 nm) of the same film before and after orientation (draw ratio of 8). (c) Fluorescence emission spectra (λ_{ex} 277 nm) of the same film after orientation. Emissions shown with polarisation parallel (0°) and perpendicular (90°) to the elongation direction. Reproduced with permission from reference ref. 46. © 2005 Wiley-VCH Verlag GmbH & Co. KGaA.

the BBS supramolecular structures (*i.e.* at high BBS concentrations) is important in the strain effect. The anisotropic distribution of the orientated films in general were then confirmed *via* fluorescence decay time measurements, quantum mechanical investigations and fluorescence spectroscopy in polarised light. For example, fluorescence spectroscopy measurements in polarised light on the film PP/BBS (0.5 wt% BBS) were found to display emission changes upon rotation of the polariser *e.g.* parallel (0°) and perpendicular (90°) to the elongation direction (Fig. 20(c)). This was found to result in the decrease of BBS monomer emission indicating the high dichroic distribution of

the BBS molecules in the orientated parts of the films. Thus the films in general were found to show deformation induced dichroic colour changes, both at high temperatures and at ambient temperatures. In some cases the colour changes were also found to be reversible occurring almost instantaneously. Also the films were able to show reproducible changes in emission intensities upon film deformation, however the films have to be irreversibly elastically deformed to achieve this.

Conclusions

As discussed at the start of this article the range of polymer responses to applied stress is large ranging from brittle plastics to soft rubbers. The majority of mechanochromic systems reviewed above have studied amorphous and semi-crystalline plastic materials though significant studies on thermoplastic elastomers and elastomers have been carried out. There are no concrete conclusions that can be reached concerning the application of fluorophores to monitor stress and/or strain in polymeric materials beyond the simple assertion that the principle has been demonstrated beyond a doubt to be feasible. As to the application of systems in monitoring or assessing mechanical deformation some are more developed than others, in particular the oligo (phenylene vinylene) derivatives work of Weder *et al.* has been repeatedly demonstrated in a range of polymer and correlation with stress has been achieved in some of these cases.^{37,40,42–44,50,51} Furthermore it is apparent that the most common and viable approach has been in changes in the excimer fluorescence of these systems, usually exhibited as significant decreases in the emission of these components. However not all fluorescent measurement techniques have been fully utilised in the development of stress–strain sensors. A recent publication described the ingenious use of fluorescence resonance energy transfer between donor and acceptor molecules dispersed in a polyether urea thermoplastic elastomer.⁵² This technique showed itself sensitive and responsive for strains up to 500%. Fluorophores are not the only component of mechanochromic systems that can be employed in stress sensing. O'Bryan *et al.* very recently demonstrated that the incorporation of a spiropyran derivative in a polycaprolactone led to colour changes upon elongation of the polymer films due to ring-opening of the spiropyran moiety.⁵³

Given the range of mechanical properties of polymeric materials none of the fluorophores used in the mechanochromic systems described is likely to be suitable for the monitoring of stress–strain across all polymer deformation responses (*e.g.* small strains of <0.5% in plastics as well as large elongations >500% in elastomers). Furthermore the nature of the system used is likely to depend upon the exact information required from the study of the polymeric material in question. For example the detection of residual stresses in an injection moulded plastic object may require an immediate highly visible optical change enabling mapping of residual stresses over a short time period and then only in model objects. Prediction and mapping of mechanical failure of polymer materials would be an important application of such mechanochromic techniques. An interesting recent example of the visualisation of crack blunting and propagation in PDMS was demonstrated by the measurement of secondary fluorescence for an embedded commercial fluorescent dye in the PDMS.⁵⁴ Whereas the long-term monitoring of a polymeric

material in an application (e.g. a polysiloxane rubber O-ring) may require a large change in optical response with deformation but have the additional requirement of long-term stability, i.e. no leaching of the fluorophore, no degradation of the fluorophore and no chemical reactions between fluorophore and the matrix. A suitable range of fluorophores now appears to be at hand to measure stress in polymers but further work is likely required to fully develop these technologies in particular the issue of long-term stability and more direct correlations of measured stresses with more classical methods allowing for optical calibration of such systems.

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