FLUORESCENT PROBES FOR SENSING PROCESSES IN POLYMERS

DOI: 10.1002/chem.200401349 *Chem. Eur. J.* **2005**, *11*, 4314 – 4325

Fluorescent Probes for Sensing Processes in Polymers

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Abstract: Fluorescence spectroscopy is an important analytical technique that has been widely used in a variety of applications, such as biomedicine, biology, and science of materials, because it presents some properties which makes it unique, that is, extraordinary sensitivity and selectivity, short delay time ($< 10^{-9}$ s), and it is neither invasive nor destructive, so it can be used for in situ measurements. Generally, intrinsic fluorescence of many materials, like polymers, is unspecific so it is not useful to analyse their properties or to be correlated to changes in their microenvironment. The incorporation of additives with fluorescent groups would be necessary. When the fluorescence emission of these molecules is sensitive to changes of properties, such as polarity, fluidity, order, molecular mobility, pH, or electric potential, they can be used for detecting such changes in their microenvironment, and they are called fluorescent probes. As long as these probes can follow processes of practical interest, they can be employed as sensors, if the information given by the measure of fluorescence adequately reflects the changes in the system. In addition, a sensor must fulfil some other requirements in order to make them of practical use, the most important being that the material support in which the sensor molecule is inserted. This support should permit a rapid detection of the process and should allow easy processing in a variety of forms. Polymers are well-known systems in which estimation of local parameters are possible by means of fluorimetric techniques. It allows the study of dynamic processes of interest, such as polymerization kinetics and mechanisms, thermal transitions, photodegradation, swelling morphology changes, and so forth.

Keywords: dynamic processes · fluorescent probes · polymers · sensors

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Introduction

Polymers are present in our lives in different ways, from a very basic container material to the most sophisticated application in new and emerging technologies. From both a scientific and industrial point of view, one of the goals of polymer science is to understand the nature and state of the polymer material in all its applications, with the objective of:

- Knowing its properties.
- Correlating the structure and properties.
- Knowing mechanism and kinetics of a given process taking place.

All of these will allow us to establish not only the features and performance (and then the applications) of the material, but also to predict the duration of a device. In addition, as it will be seen later, this knowledge will permit the design of new tools.

The processes that could take place in a polymeric material are diverse, but from a practical point of view we summarize here some that could affect the physical properties of a material:

- Chemical reactions, such as polymerization (curing), cross-linking, functionalization, or secondary reactions.
- Ageing, and thermal, photochemical, or chemical degradation.
- Transport of small molecules, such as water, solvents, and chemicals (additives).
- Thermal transitions (relaxations, T_g).
- Change of morphology (microphases separation, crystallization, orientation).
- Self-assembly, gelation, and gel swelling.

All these processes involve changes in the material at the molecular level. To follow them, there are many useful techniques, among the most used are: spectroscopic methods (UV-Vis, FT-IR, Raman, NMR), thermal methods (DSC, DMTA), gravimetry, microscopy, mechanical tests, and chemical analysis. Although these techniques provide valuable information about polymer materials, some disadvantages arise from the necessity of sampling or the destructive-

ness of the tests, or even the lack of sensitivity. Most of them are not suitable to follow processes in situ.

Among the techniques available, fluorescence spectroscopy has become a powerful tool to monitor microscopic changes in polymer systems. This is due to several advantages of fluorescence with respect to conventional techniques:[1]
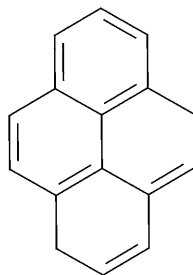
- High sensitivity.
- High selectivity.
- Short response time ($<10^{-9}$ s).
- Sampling not needed.
- Nondestructiveness.
- Processes occurring at different timescales could be studied in real time.

Figure 1. Pyrene and its fluorescence spectra in *n*-hexane and acetonitrile (adapted from reference [46]).

A disadvantage is that intrinsic fluorescence of polymeric materials is usually very weak and appears in an unspecific wavelength range, if it exists at all. Therefore, the addition of a fluorescent molecule that can give information about the processes in its microenvironment is required. These molecules are called fluorescent probes.

There are several requirements that a fluorescence molecule must fulfil to be used as probe, and the first is that at least one fluorescence parameter should change depending on the conditions of its environment. The methods used to measure fluorescence changes of probes include steady-state, anisotropy, and time-resolved measurements. Among these, the parameters that have been proven adequate to correlate changes in the medium with fluorescence are monomer/excimer ratio, maximum emission wavelength, intensity at the maximum wavelength, fluorescence intensity ratio between two wavelengths, fluorescence lifetime, fluorescence area, and the first moment of fluorescence. The selection of the fluorescence parameters that best represents the variation in the medium depends on the system, and examples of this will be given below.

Usually, the changes in polymeric materials that can be easily studied by fluorescence are related to rigidity of the medium (viscosity, free volume, mobility of chains, ageing) or to polarity (microphases and domains, transport of small molecules, reactions, ageing).

The families of fluorescence probes usually employed under these circumstances are:

1) Compounds that may form dimers in the excited state (excimers), which have different fluorescence emission from the single molecule (e.g. aromatic hydrocarbons, especially pyrene, and derivatives, Figure 1). This needs two fluorophores to move through the medium to be sufficiently close to form an excimer; the process is strongly
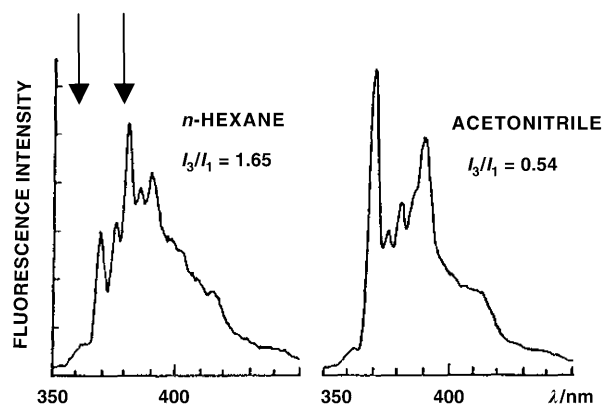
viscosity dependent. Additionally, pyrene shows significant fine structure due to vibrational relaxations, the relative intensity ratio of which decreases with an increase in polarity of the solvent.

2) Systems that undergo energy transfer between two chromophores, in which the energy is transported from a donor in the excited state (D*) to an acceptor in the ground state (A) (Figure 2). The process could be radiative (trivial energy transfer) or nonradiative (Förster or Dexter energy-transfer mechanisms); the latter being more important because it is dependent on the distance between chromophores.

3) A single probe exhibiting multiple fluorescences depending on the environment. This group includes molecules which exhibit emissive properties that depend on internal rotation; these are called molecular rotors (Figure 3). Internal rotation of at least one single bond of the molecule is the main route for nonradiative deactivation. Hence, an increase in viscosity around the probe reduces this process by frictional resistance thus resulting an increase in quantum yield.
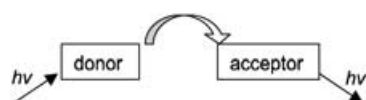

Figure 2. Energy transfer between two chromophores.

Full description of the mechanisms for fluorescence variations of probes are profusely reviewed in the literature.[2]

Processes Measurable by Means of Fluorescence Probes

As commented before, most of the processes of practical importance can be related to changes in viscosity and/or polarity in the microenvironment of the probe. This revision does not intend to be exhaustive, but to give a general overview of the different processes that could be monitored by fluo-

rescence of probes inserted in polymer systems. An excellent and complete revision of fluorescence probes for materials science can be found in specialized monographs.[3]

Polymerization: One of the most studied processes in polymers with fluorescence probes has been the polymerization reaction, since the mechanical and chemical properties of the formed materials strongly depend, among various factors, of the degree of cure.

The polymerization reaction is a relatively complicated reaction that transforms a monomer (or mixture of monomers) into a polymeric chain. Basically, and depending on the chemical functionality of the monomers, it could take place through two different mechanisms: 1) a chain reaction (addition of monomer at the end of the growing chain) or 2) through a stepwise reaction. Depending on the functionality of the monomer, the resultant material could be a linear or branched soluble polymer, or a cross-linked insoluble network. The mechanisms and kinetics of both types of processes are very different, but the system always undergoes a transformation from a viscous or fluid liquid to a rigid vitreous material, so viscosity-sensitive probes will be very useful for following them.

Since the pioneering work of Loutfy[4] describing the fluorescence–viscosity dependence of malononitrile probes, a lot of research groups have studied the kinetics of polymerization through fluorescence probes. Most efforts have been devoted to acrylic monomers given their industrial importance.

Polymerization of methyl methacrylate (MMA) was monitored by means of pyrene-labeled alkanes by Wang and co-workers in 1984,[5] measuring the monomer/excimer ratio of pyrene chromophore as a function of time. Neckers described for the first time the linear relationship of pyrene fluorescence ratio with the rate of MMA polymerization at low conversions.[6]

Peckcan et al. measured pyrene (Py) intensity along MMA polymerization, and found a sudden increase of Py intensity from a certain point of the reaction-time profile, that they used to determine the gel point of the system (point at which the system vitrifies) as a function of reaction temperature, the probe being insensitive after this point.[7] They also measured conversion of monomer in the cross-linking copolymerization of styrene–divinylbenzene up to vitrification[8] (Figure 4).

However, pyrene has the disadvantage that a certain fluidity of the medium is needed to allow the two Py molecules to diffuse and encounter to form the excimer, so it is not an adequate probe to follow the polymerization reaction until final conversion.

Neckers and co-workers studied the photopolymerization of acrylics for more than 15 years. They have described different probes, most of them from molecular rotor families[9] (Figure 5).

Our group have described the synthesis of several monomeric and polymeric fluorescent probes,[10] and they have been used for monitoring the photopolymerization reaction
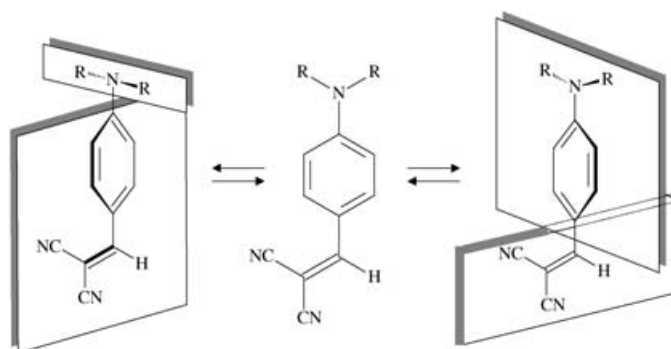

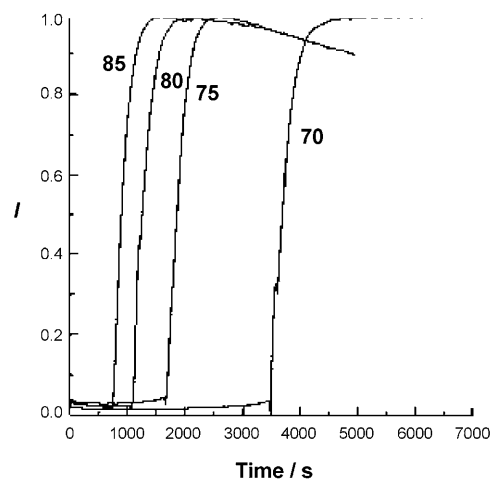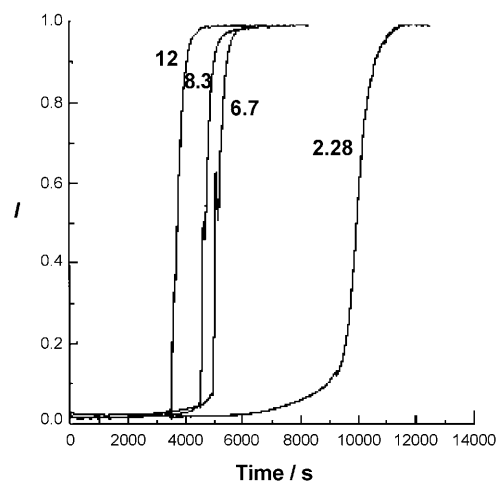Figure 3. Internal molecular rotation around σ-bonds of molecular rotors (adapted from reference [2b]).

Figure 4. Plots of Py intensity, *I*, against reaction time, *t,* during St-DVB copolymerization, at different DVB content (top) and temperature (bottom) (adapted from reference [8]).

of acrylics (Table 1). Kinetic profiles and instantaneous monomer conversion have been measured up to the limiting conversion (Figure 6).
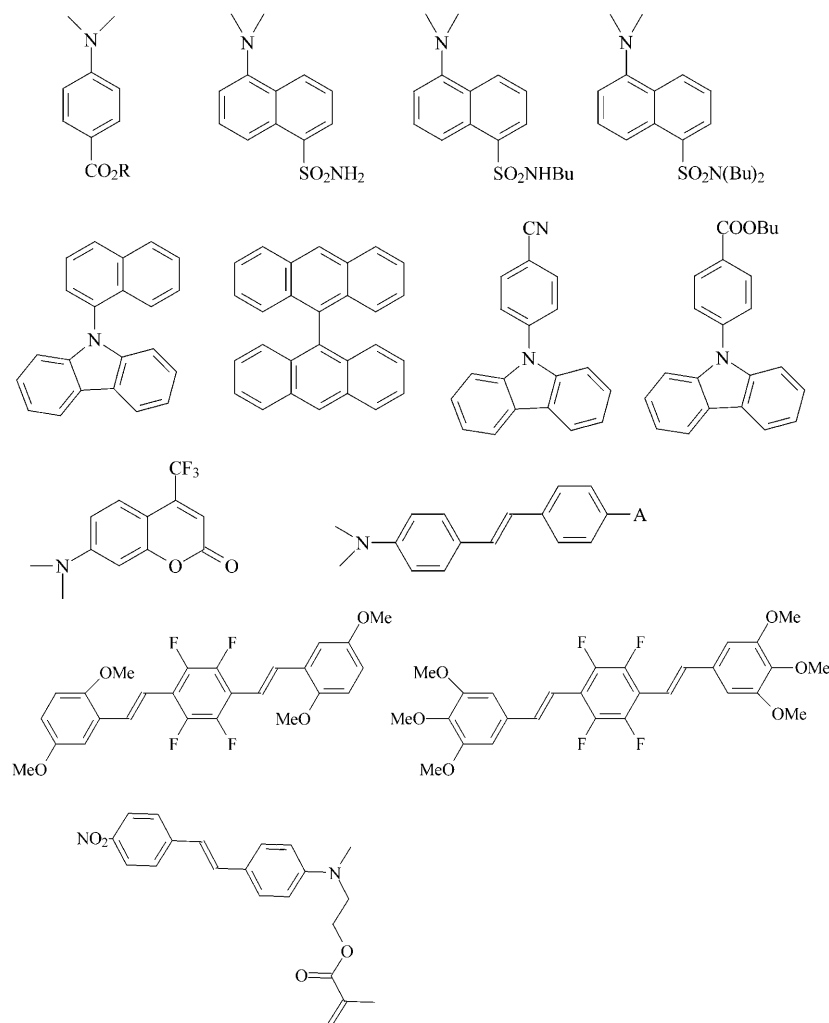
Figure 5. Some of the probes studied by Neckers et al. in polymerization reactions.

In addition, several other features of the reaction such as influence of oxygen inhibition,[11] secondary reactions caused by initiator,[12] gel-point determination,[13] and variations in free volume during polymerization[14] have been determined (Figure 7).

The good response of the probes to the changes in viscosity/rigidity makes them useful for following very fast reactions and for elucidate their mechanism, such as the case of the pulsed laser polymerization reaction.[11,15] The influence of pulse frequency on the rate of polymerization and limiting conversion is easily determined in processes that take place in less than 30 s (Figure 8).

Besides radical chain polymerization, polymerization of thermosetting compounds has been also studied by fluorescence methods, but almost all the work is restricted to epoxy systems.[16]

Strehmel et al.[17] studied the cross-linking reaction of a conventional epoxy resin (DGEBA, diglycidyl ether of bisphenol A) through the fluorescence decay time of two rotor type molecules. Even though they found certain agree-

ment with conventional methods for detecting the gel point, the high free-volume required for those probes for internal rotation make them not very sensitive (Figure 9).

One of the most active groups in epoxy systems has been Baselga and co-workers. In addition to kinetic profiles and gel-point determination, they have correlated fluorescence with chemical transformations of the reaction mixture, such as reaction of the primary, secondary, and tertiary amino groups, and the maximum concentration of secondary amino groups in the reaction mixture[18] (Figure 10).

When curing glass or silica fibers reinforced epoxy systems, they also were able to observe differences between the curing reactions of the fiber–epoxy interface or the bulk material.[19]
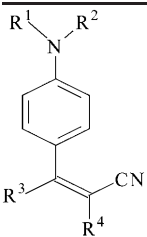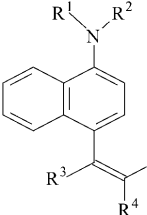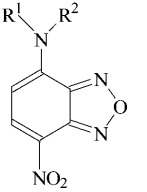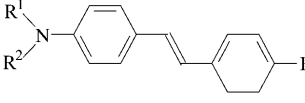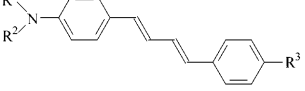
Microenvironment: The ability of the fluorescent probes to detect changes in its microenvironment polarity is a powerful tool for investigating many aspects of polymer structural changes. Many investigations make use of the solvato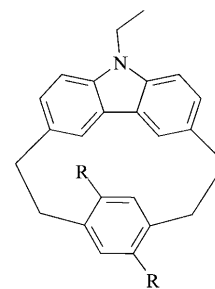chromic shift experienced by fluorescent dansyl derivatives to correlate it with structural changes in polymers (Figure 11).

Carlier et al.[20] studied site accessibility of different polymer-supported samples by grafting dansyl chromophore to silica or to the polymer chain. Swelling the samples and comparing the experimental emission wavelengths with those in pure solvents, they described differences in site accessibility between linear and cross-linked polymers depending on the nature of the solvent.

Swelling of polymers and gel formation have been extensively studied by means of fluorescent probes. Peckan prepared disc-shaped PMMA by free radical cross-linking polymerization in the presence of pyrene, and studied the swelling and release kinetics as a function of cross-linking density, measuring Py fluorescence intensity.[21] More recently, these authors measured lifetimes of Py in order to estimate the cooperative diffusion coefficient for the swelling process and the desorption coefficient for the drying process of polystyrene (Figure 12).[22] Interpenetrated polymer networks have also been studied.[23]

Table 1. Rotor-type probes for monitoring polymerization reactions.

Probe	R^1	R^2	R^3	R^4
(aminophenyl acrylonitrile)	Me	Me	H	CN
	Me	Me	CN	CN
	Et	CH_2CH_2OH	CN	CN
	Et	$CH_2CH_2OC(O)CH_2{=}CH$	CN	CN
	Me	Me	H	$CONH_2$
	Me	Me	OMe	$CONH_2$
(aminonaphthyl acrylonitrile)	Me	Me	H	CN
	Me	Me	OMe	$CONH_2$
(benzoxadiazole, NO_2)		Et		
	Et	CH_2CH_2OH	–	–
	Me	$CH_2CH_2OC(O)CH_2{=}CH$	–	–
	Me	Me	–	–
		Me		
(aminophenyl stilbene)	Me	Me		–
(aminophenyl diene)	Me	Me	NO_2	–

The donor and acceptor moieties of the cyclophane suffer little structural changes over wide viscosity and temperature changes, thus allowing the correlation of the fluorescence only to polarity changes. This probe can detect even small changes in the dielectric constant at transition temperatures in polymer solids and provides a means by which to determine the dielectric constant that result from high-frequency motions of polar groups.

Studies on phase separation and morphology of blends have also been undertaken by using the microfluorescence technique of doped systems.[29]

The very distinct environmental polarity in micellar systems has been studied by inclusion of polarity sensitive probes, assuming that their fluorescence response will change when the probes are solubilized in polar or apolar environments.[24] Winnik and co-workers have used changes in fluorescence spectra to deduce the apparent critical micellar concentration (CMC) of block copolymers,[25] and Webber et al. measured lifetime and quenching of emission of systems doped or labeled with probes.[26]

Labeling polymers with a probe can give information about conformational changes of the polymer chains. Tsuneda et al. grafted the dansyl group to a polyethylene microfiltration membrane, and evaluated the solvent effect on the conformation of the PE chains and its relationship with solvent permeability through the membrane.[27]

The problem presented with probes that show multiple fluorescence depending on their microenvironment is that often both fluorescence types are present in the spectra. Then it could be difficult to correlate the emission of the probe in solid polymers with its reference emission in solution. Recently Ito and co-workers have overcome this disadvantage by synthesizing an exciplex forming a rigid cyclophane (shown here), which allowed them to measure changes in dielectric constants of polymer solids.[28]

Chain mobility and thermal transitions: Even though a lot of D-π-A intramolecular charge-transfer probes have been described for viscosity sensing, few examples of D-σ-A probes appear in the literature. Jenneskens and Verhoeven investigated the mobility of surrounding matrix sites with a piperidine derivative (illustrated here) and found a correlation with polymer molecular weight, attributed to differences in medium reorganization within the photophysical timescale.[30]
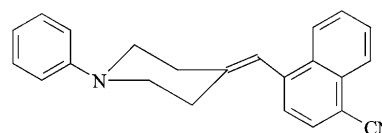
In addition to the glass transition (T_g), secondary relaxations of semicrystalline polymers are thermal transitions that involve cooperative motions of macromolecular segments. These processes can be studied by means of fluorescence spectroscopy of doped polymer films, taking into account that the emission of the probe will decrease as long as a decrease of the rigidity of the polymer takes place as a result of segmental motions.[31]

Figure 8. Fluorescence variation versus number of laser pulses for a pulsed-laser photoinitiated polymerization of an acrylic formulation. Variation of rate of polymerization (slope) and limiting conversion (plateau) is observed for the different pulse frequencies employed (adapted from reference [15]).
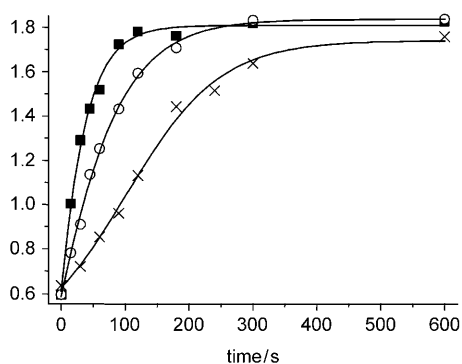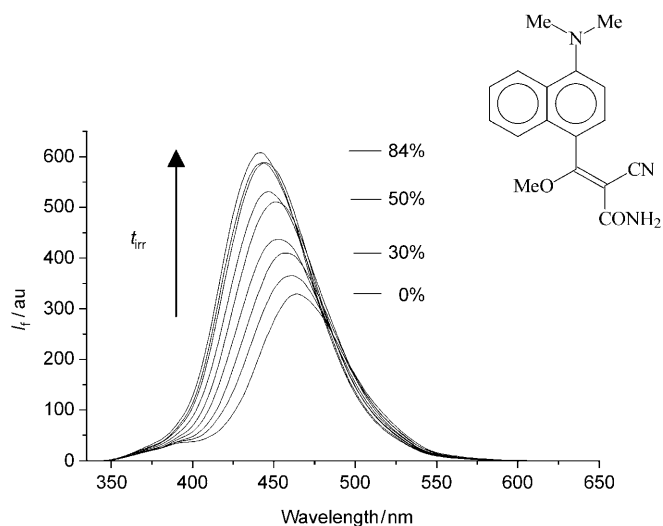

Figure 6. Fluorescence spectra variation (top) and kinetic profiles (bottom) for the photoinitiated polymerization of lauryl acrylate. Below the fluorescence is measured as $F = I_f(438 \text{ nm})/I_f(475 \text{ nm})$. (■) $I_0 = 0.55$ mcal s^{-1}; (○) $I_0 = 0.11$ mcal s^{-1}; (×) $I_0 = 0.03$ mcal s^{-1} (adapted from reference [8]).
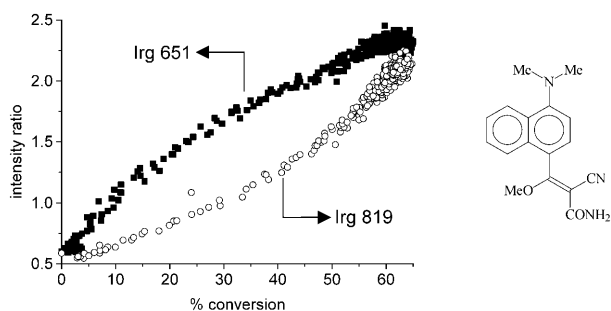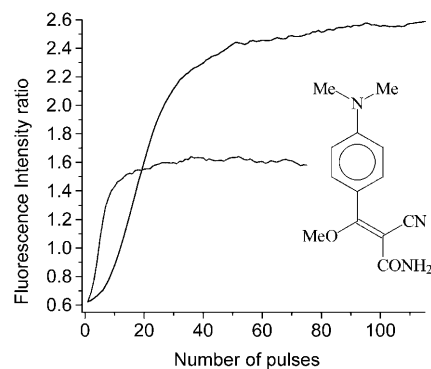

Figure 7. Fluorescence-conversion profiles for a photo-cross-linkable acrylic formulation depending on the photoinitiator used. Different reaction behavior is attributed to secondary cross-linking reactions (adapted from reference [12a]).

Stresses and mechanical properties: The control of distribution of stress in polymer materials is very important in order to anticipate and prevent catastrophic failure during the working life of the polymer. Currently, there are several
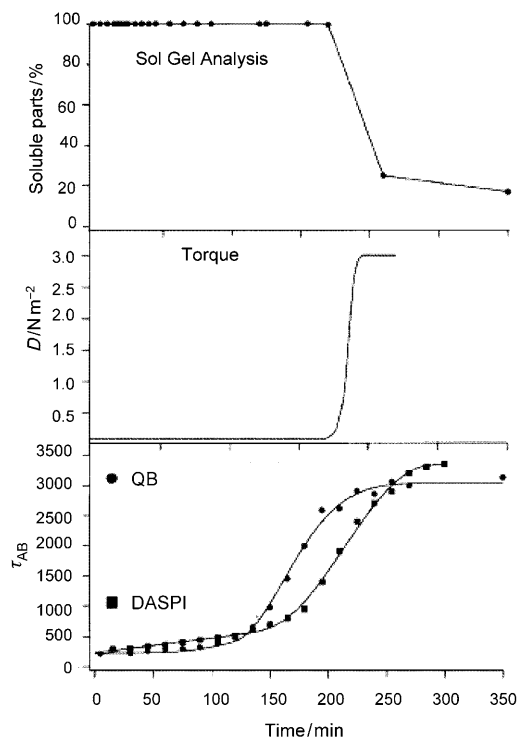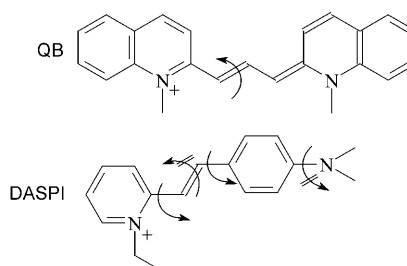

Figure 9. Comparison of the time-resolved fluorescence data (τ_{AB} in ps) obtained from QB and DASPI with other methods (sol-gel analysis and torque measurements), for the curing reaction of DGEBA-DDM (adapted from reference [17]).
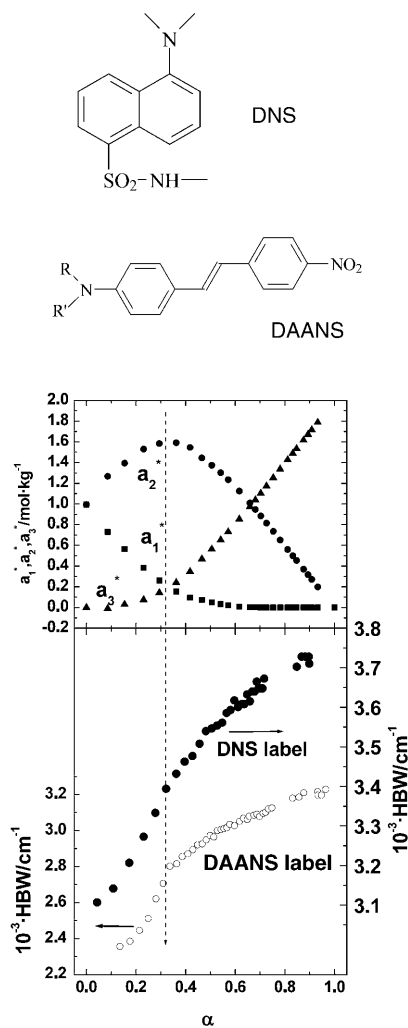
Figure 12. Plots of pyrene lifetime versus swelling (top) and drying time (bottom) of disc-shaped polystyrene gels (adapted from reference [21]).

Figure 10. The dependence of the primary (*a*1), overall secondary (a*2), overall tertiary (a*3) amino groups concentration (top) and the half bandwidth (HBW) (bottom) for the DNS And DAANS labels on the epoxy group conversion (adapted from reference [18]).
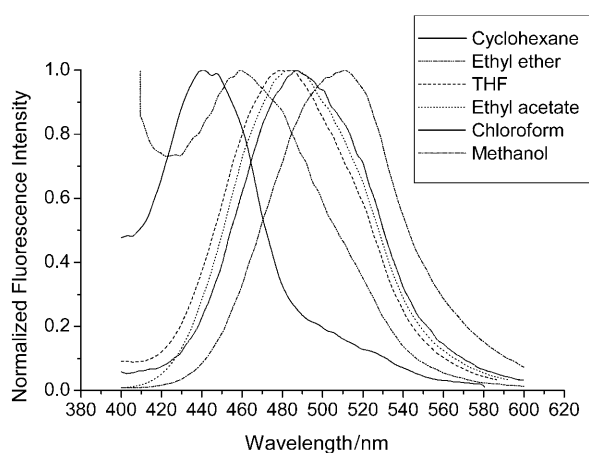

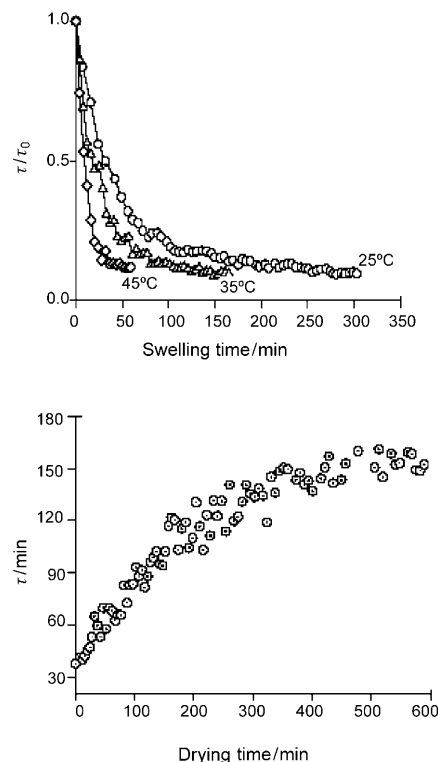Figure 11. Emission spectra of dansylamide in different solvents.

methods for testing mechanical properties, but all of them need specimens that have been prepared with defined geometries and the tests are done ex-situ. Fluorescence of doped systems appears to be an alternative method if it could give a specific response to mechanical deformation of polymers.

The effect of deformation (stretching) of an epoxy resin on the fluorescence of probes has been studied.[32] When mapping fluorescence (taken as the first moment of fluorescence, $\langle \nu \rangle$) for an uniaxially stretched sample, the highest value of $\langle \nu \rangle$ suggests that there is an accumulation of stress in the centre of the specimen along the load axis (Figure 13). This method has been also applied to study mechanical strength of these materials.[33]

Degradation: Prediction of useful life of the materials is a major challenge for polymer industry. The degradation of polymeric materials is caused by exposure to various factors such as heat, light, mechanical stress, and microorganisms. The mechanism of polymer degradation is extremely complicated, involving simultaneous formation and decomposition of hydroperoxides. Several techniques are usually used to study the mechanism of polymer degradation. Recently, a sensitive fluorescence-based method has been developed in order to assess physical or chemical changes in the early stage of the photodegradation of polyurethane–acrylate adhesive.[34] Two fluorescent probes, *p*-dimethylaminosalicylic acid (*p*-DASA) and Oregon Green (OG), incorporated into
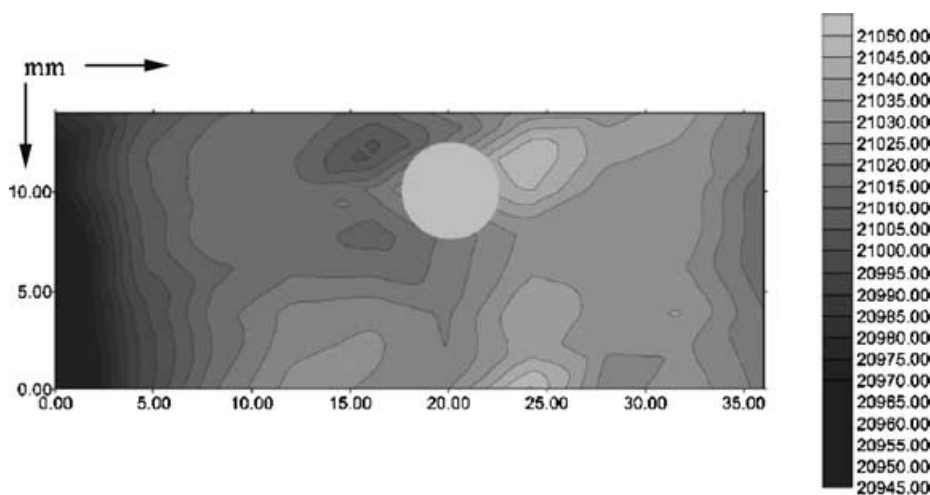
Figure 13. Fluorescence mapping of an uniaxially stretched epoxy resin formulation, showing accumulation of stresses in the bulk material (adapted from reference [32]).

the adhesive formulation were sensitive to the formation of oxidation products. During photodegradation a rapid decrease of the emission was observed, attributed to the formation of oxidation products (peroxide, etc.) during photodegradation that are able to quench the excited states of emitting fluorophores. As the kinetics of this process can be measured well before any defects become visible in the adhesive, the technique is a valuable method to analyse photodegradation in its initial stages.

Moisture, ion, and small-molecule sensing: The detection of chemicals in a given medium is a process that has enormous implications in wide range of chemical and biological processes and has been the driving force for the study and design of specific sensors. Fluorescence probes have been used for this purpose for some time.

A sensor must fulfil some requirements that make it of practical use, one of the most important being the nature of the material support in which the sensor molecule is inserted. This support should permit a rapid detection of the process and should allow easy processing in a variety of forms. Amorphous polymers are materials permeable to small molecules, so estimation of local parameters can give accurate information about the penetrant. The specific role of polymer materials in sensor applications has been recently reviewed.[35] Fluorogenic and chromogenic sensors for anions have been also recently reviewed.[36]

When a small molecule penetrates into a polymer film, the following parameters will mainly change: polarity, mobility of the chains ("plastification"), and specific interactions that are established between the penetrant and functional groups present in the polymer.

Interesting work is currently being undertaken with the dansyl chromophore as its sensitivity to polarity changes.[37] Recently, the dansyl chromophore was used to label dendrimers, with a view to the observation of signal amplification of such systems. Balzani reported the quenching of the

dansyl fluorescence when protons or ions are entrapped in the dendrimer topology, and bind to specific sites of the interior of the dendrimer architecture[38] (Figure 14).

Quenching of fluorescence is not a very good strategy for sensing, because a decrease in emission could be related to other experimental facts rather than the presence of the target molecule.

In addition to the polarity- and viscosity-sensitive fluorophores described in this paper, the probes for which the fluorescence depends on photoinduced electron transfer (PET) are very useful for small-molecule sensing when a specific interaction takes place. It is possible to design signalling units in which, in the absence of the analyte, a PET process deactivates fluorescence emission; this can be subsequently reversed when a molecule coordinates or binds a specific site[39] and emission increases (Figure 15).

In this sense, acridine[40] and naphtalimide[41] amino derivatives (shown here) have been proven to give very good results, for both cation and pH sensors.
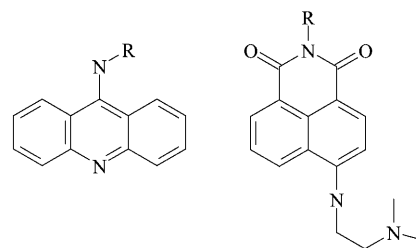
Water sorption is a well-known problem that causes deterioration of the final properties of a polymer material and, thus, it is related to its useful lifetime. Great efforts have been undertaken to follow the effect of moisture in polymers and different techniques have been used for two purposes: 1) to determine the content of water and 2) to investigate the mechanical properties of the material after exposure to humid environments.[42] In an attempt to develop optical sensors, fluorescent probes have been added to polymers to be used as humidity sensors.[43] Water acts as a softening agent increasing the space between polymer chains and producing a plasticizing effect. In general, the presence of water increases the mobility in the polymer matrix decreasing fluorescence emission of mobility-sensitive or rigidochromic fluorescent probes.
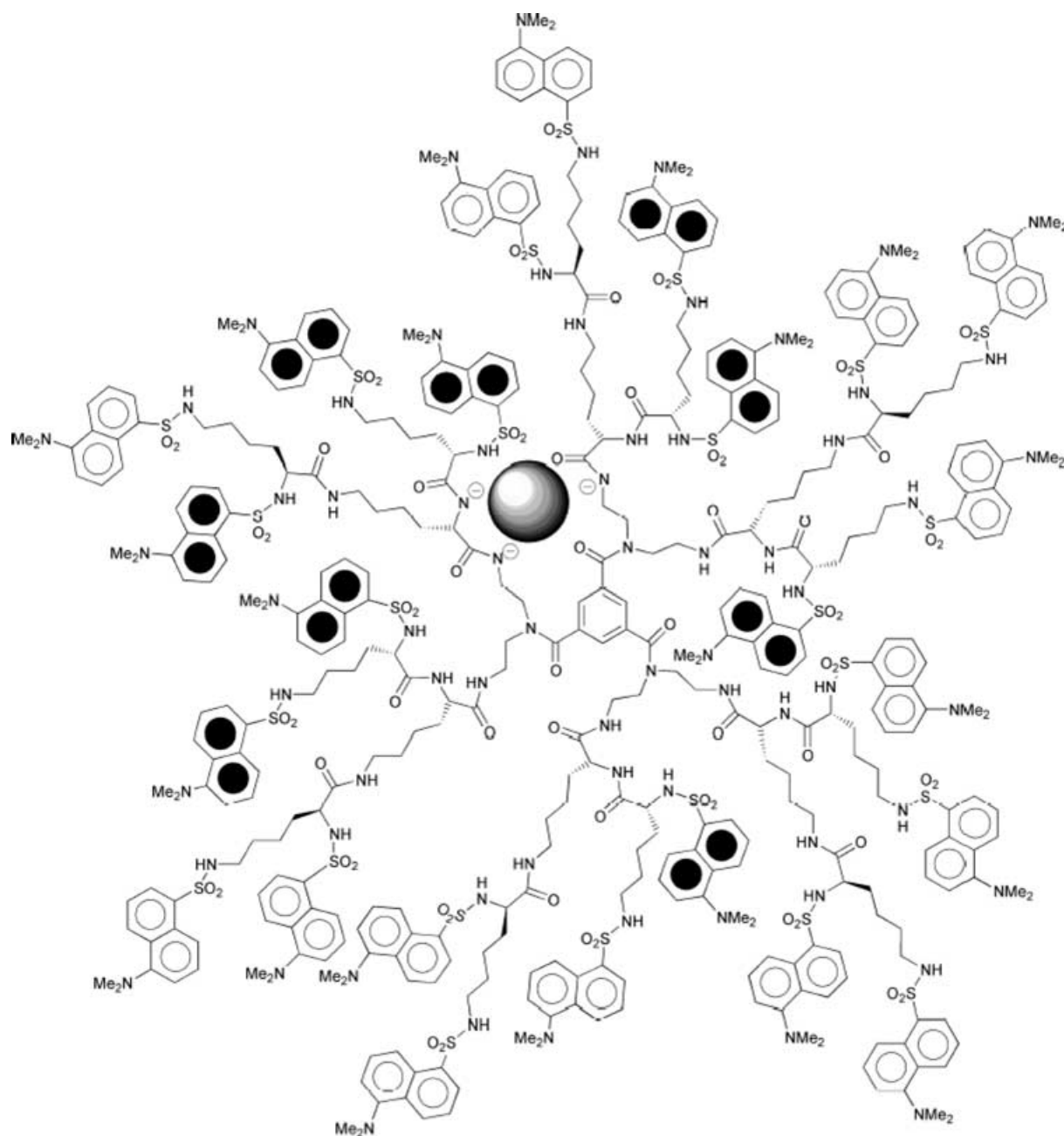
Figure 14. Coordination of metal ions in the interior of a dendrimer structure and quenching of dansyl fluorescence. The supposed quenched dansyl units are labeled black (adapted from reference [38]).

Torkelson has reported the use of 4-tricyanovinyl-[*N*-(2-hydroxyethyl)-*N*-ethyl]aniline for quantitative monitoring of water up-take in polymeric coatings.[44]

We have been also able to calculate the diffusion coefficient of water in different polymeric films doped with a fluorescent probe (Figure 16). Assuming that the observed decrease in fluorescence emission is proportional to the water uptake of the film, and by modifying Fick's equation we have obtained a good agreement with diffusion coefficients calculated by the conventional gravimetry method.[45]

Concluding Remarks

Fluorescence probe methods are very useful for monitoring processes in polymers, because its high specificity, selectivity and short response time, with the additional advantage that they can be used for in situ measurements. Sensing at molecular level provides information about changes in the microscopic environment of the probes. The variations that most affect the fluorescence emission of a probe are usually related to changes in polarity, rigidity, or specific reactions with the fluorophore.
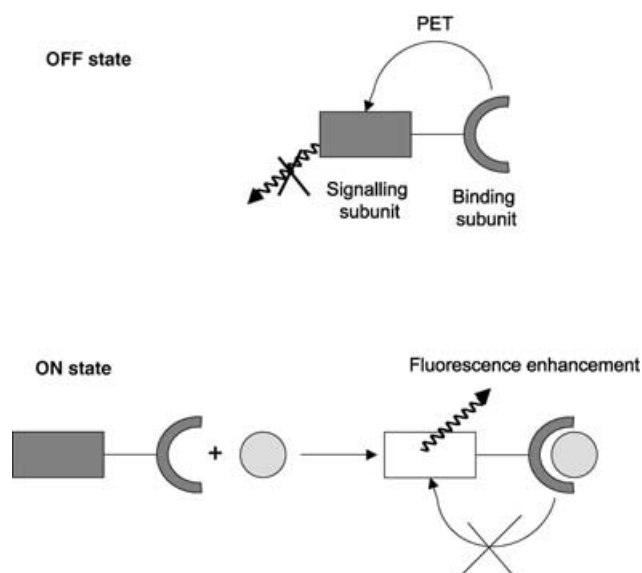
Figure 15. Mechanism for small-molecule sensing when a specific interaction between fluorophore and analyte takes place (adapted from reference [39]).
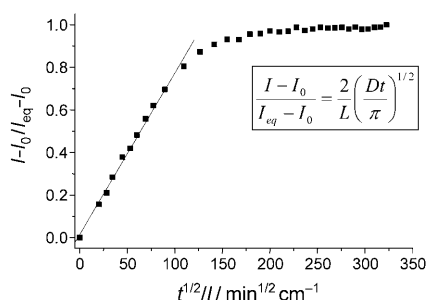

Figure 16. Fluorescence variation versus immersion time in water for water diffusion coefficient calculation. Inset: modified Fick's equation used for calculation.

$$\frac{I - I_0}{I_{eq} - I_0} = \frac{2}{L}\left(\frac{Dt}{\pi}\right)^{1/2}$$

The photophysics of the main families of fluorophores are now well established, and the instruments to monitor emission have been developed and are easy to operate; therefore the technique is now available even for scientists who are not specialists in this particular area.

Results from fluorescence measurements can be correlated with those obtained by other conventional macroscopic methods; in fact, the good correlations found for most processes corroborate the excellence of fluorescence as monitoring technique. Moreover, if the results from fluorescence measurements differ from those obtained by other methods, some considerations should be made. After setting aside the fact that specific photophysical processes or degradation of the probe (through chemical, thermal, or photochemical reactions) could have taken place, the possibility that the changes observed respond to a different microscopic process should be taken into account. In this sense, processes involving different mechanisms or reactions that take place simultaneously can be detected by fluorescence (for instance,

double-bond reaction and macroradical coupling through hydrogen abstraction in polymerization reactions).

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