Temperature Dependence of Fluorescent Probes for Applications to Polymer Materials Processing

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We have examined the temperature dependence of fluorescence spectra from dyes that can be used as molecular probes during polymer processing. The dyes, perylene and benzoxazolyl stilbene, are in a class of dyes called band definition dyes, so called because their fluorescence spectra contain distinct intensity peaks at characteristic wavelengths. The dyes were chosen for this study because they are soluble at dopant levels of concentration in organic polymers at elevated temperatures and they survive without degradation at polymer processing temperatures up to 300 °C. Changes induced in the fluorescence spectra over a range of typical processing temperatures were examined using statistical techniques that establish correlations between fluorescence intensity, wavelength, and temperature. The derived correlations are the basis for temperature calibrations that can be applied to process monitoring. A phenomenological model that assumes temperature dependence for both nonradiative and radiative decay modes is developed. A fit of the model parameters to the fluorescence spectra yielded activation energies for the temperature dependence of fluorescence decay rates.

Index Headings: Fluorescence spectroscopy; Fluorescence decay rate; Spectral temperature dependence; Nonradiative decay; Polymer processing.

INTRODUCTION

Employing fluorescent dyes as temperature probes has been the subject of a number of studies in the literature.¹⁻¹² Both time-resolved and steady state fluorescence measurements have been employed. Most of these investigations were limited to aqueous solutions or solvent media of low viscosity. However, our motivation for studying fluorescent probes is to use them as temperature probes during the processing of polymer materials, an application that presents severe environmental conditions because of elevated temperatures and relatively long machine residence times involved. Most polymer processes are carried out at temperatures between 200 and 300 °C, and for some engineering resins temperatures up to 370 °C are used. Machine residence times are on the order of several minutes or more, requiring that degradation kinetics of the fluorescent molecule must be slow in order for it to play a useful role as a temperature probe.

Obtaining accurate and true resin temperatures during polymer processing has been problematic for many years.¹³⁻¹⁵ This is because conventional temperature sensors such as thermocouples, thermistors, and radiometers have difficulty distinguishing between machine temperature and resin temperature. For extrusion processing, thermocouple sensors are placed in machine instrumentation ports where heat transfer from the machine to the thermocouple junction is much more efficient than is heat transfer from resin to thermocouple.¹⁶ In addition, the large thermal mass of the machine damps the response of the thermocouple. Infrared radiometry can yield accurate resin temperatures for transparent resins of known emissivity, but problems exist for the calibration of this instrument should the resin emissivity change, as with a filled resin. The assumption that a flowing resin has the same temperature as the machine is erroneous because a viscous resin undergoing flow dissipates energy in the form of heat, a phenomenon called shear heating. For even moderate shear rate and viscosity, the effect can be quite significant, raising resin temperature tens of degrees above the machine set point.¹⁶

The inadequacies of temperature measurements have major implications regarding rheological understanding of polymer processing and the onset of resin degradation temperatures. To address these issues we have engaged in a program to use fluorescence spectroscopy as a tool for monitoring resin temperature during processing. Most polymers are not inherently fluorescent, making the addition of a fluorescent dye to the polymer matrix necessary. Compounding small quantities of additives such as pigments or anti-oxidants with a commercial polymer product is a standard processing procedure that can also be employed to mix fluorescent dye and resin. Dopant concentrations of dye in resin are used, less than 10^{-5} mass fraction of dye in the resin. A low concentration ensures that solubility of dye in resin is achieved, that dye-dye molecular interactions are minimized, and that the dye molecule is surrounded by a medium of resin molecules. The concept regarding fluorescent dyes is that they are molecular probes, i.e., they respond to the molecular environment in which they exist and report the conditions of that environment via their observed spectra. Thus, a temperature deduced from fluorescence spectra is a true resin temperature.

Many researchers have used excimer-producing fluorescent dyes to measure temperature. One such dye is bis(-pyrene) propane (BPP), for which intramolecular rotational motion is the basis of the dye's temperature response.^{1,3,5,7,8,11,17} In previous studies, we used BPP to monitor polymer injection molding and to measure temperature gradients in an extruded resin flow stream.^{1,18,19} However, BPP is somewhat limited in application to polymer processing because it is susceptible to photobleaching and because it degrades at temperatures above 220 °C. In the search for fluorescent dyes that can be used at higher processing temperatures, we identified a new class of temperature sensitive dyes that we call fluorescent band definition dyes.¹⁶ In contrast to the mobilitybased photochromic activity of excimer-producing dyes such as BPP, temperature sensitivity of band definition

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benzoxazolyl stilbene (BOS)









(BTBP)

FIG. 1. Molecular structures of BOS, perylene, and BTBP.

dyes is quantum mechanical in origin and depends on the temperature dependence of decay from an excited state to an energy level in the ground state.

In this paper we will describe the performance of three band definition dyes, benzoxazolyl stilbene (BOS), perylene doped into polycarbonate and studied under conditions comparable to polymer processing, and bis(di-tert butylphenyl) perylenedicarboximide (BTBP) doped into polypropylene. Perylene has been used extensively in the colloidal and biological sciences to monitor rotational dynamics and quenching associated with chemical diffusion.²⁰⁻²⁹ BOS has a quantum efficiency of 1 and has a large molecular geometrical anisotropy that lends itself to studies of orientation in stretched polymer films.³⁰⁻³⁵ BOS is non-toxic and is used in commercial packaging applications where it is valued for its deep blue color. BTBP is a large molecule that possesses sizable geometric asymmetry.³⁶ We have used it for temperature and fluorescence anisotropy measurements.³⁷

EXPERIMENTAL

Fluorescent dyes for polymer process monitoring are chosen using these criteria: (1) they must survive the high temperature and long residence times used for processing; (2) their spectra must show significant changes with respect to temperature; (3) the wavelengths of excitation

and emission must be in the near ultraviolet or visible range; (4) they must be soluble in the resin; and (5) they must be chemically inert. The first criterion, survival at high temperatures, is the most challenging and has eliminated many dyes that we have examined from consideration. For organic dyes, solubility in the resin is usually not an issue because we work at very low concentrations of dye, less than 10⁻⁵ mass fraction of dye in the resin. Also, solubility is enhanced at high processing temperatures. The molecular structures of three dyes that satisfy these criteria, perylene, BOS, and BTBP are shown in Fig. 1. The dyes are band definition dyes and were obtained from Aldrich Chemicals.† The excitation wavelength for pervlene is 410 nm with fluorescence emission from 430 to 530 nm; for BOS, excitation is 365 nm with fluorescence extending from 390 to 470 nm; for BTBP, excitation is 488 nm with fluorescence extending from 500 to 650 nm. We have used perylene and BOS up to 300 °C in process monitoring applications without observing degradation. Degradation was monitored by observing the spectrum of the dye doped into polycarbonate during temperature cycling between 150 and 300 °C. Absence of degradation was achieved if no change in the spectral curve occurred during temperature cycling, as was the case for perylene and BOS after three temperature cycles to 300 °C. Our experience with BTBP has been limited to temperatures below 270 °C in a polypropylene matrix, for which we observed no evidence of degradation after one cycle to 270 °C.

For the experiments described below, perylene and BOS were doped into polycarbonate (DOW Chemical 200-10).[†] Doping of polycarbonate was carried out using a common solvent, dichloroethylene, and subsequently evaporating off the solvent. For BTBP doped into polypropylene (Fina 3371),[†] doping consisted of pouring a solution of BTBP in toluene over resin pellets, evaporating the solvent, and then mixing the dye-coated pellets in an extruder or batch mixer at 200 °C. We prepared polymer specimens with mass fractions of dye in the polymer that were between 2×10^{-6} and 6×10^{-6} .

Spectral characterization of the dyes was carried out in a temperature controlled cell consisting of an aluminum block with a finger well with a capacity for 10 g of material. Optical access to the cell is via fiber-optic probe, as shown in Fig. 2. The essential elements of the measurement system are a xenon arc lamp light source that is filtered to the excitation wavelength of the dye being used, the temperature cell, a bifurcated bundle of 100µm-core optical fibers, half of which transmit light to the specimen and the other half of which collect fluorescence and transmit it to the detector, and a grating monochromator with photomultiplier detection. Entrance and exit slits were set at 0.25 mm, yielding 1 nm wavelength resolution. The spectra presented here are uncorrected for transmission characteristics of the optical fibers, monochromator, and photomultiplier detector.

[†] Identification of a commercial product is made only to facilitate experimental reproducibility and to describe adequately the experimental procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experiment.

optical fibers



FIG. 2. A schematic of the experimental apparatus.

RESULTS

Consider the spectra in Figs. 3 and 4 obtained at atmospheric pressure for perylene and BOS in polycarbonate where the relative uncertainty in the intensity measurements is 0.2% and the standard uncertainty in the temperature is 1 °C. Distinct bands, seen at 452 and 476 nm for perylene and 412 and 434 nm for BOS, are associated with excited state decay to different energy levels in the ground state. Although there is a continuum of energy levels in the electronic ground state, there is enhanced population associated with decay at 452 and 476 nm (perylene) and 412 and 434 nm (BOS). The basis of the temperature sensitivity of the fluorescence decay is the temperature and wavelength dependence of the probability of decay from the excited state to the ground state. This dependence is seen in changes in the shape of the spectrum, particularly the disappearance of the trough between 452 and 476 nm (perylene) and 412 and 434 nm (BOS) as temperature increases. Similar results are shown in Fig. 5 for BTBP doped into polypropylene, where the two peaks of interest are at 528 and 565 nm with the trough between them at 548 nm.

The similarity between the perylene, BOS, and BTBP



FIG. 3. Intensity vs. wavelength for BOS doped into polycarbonate for temperatures 152, 180, 212, 240, 270, and 300 $^{\circ}$ C.



FIG. 4. Intensity vs. wavelength for perylene doped into polycarbonate for temperatures 180, 203, 225, 249, 269, and 295 °C.

spectra and their temperature dependence is obvious. The data of Figs. 3, 4, and 5 demonstrate the generality of the band definition phenomenon. We have observed the same effects for many band definition dyes, for example, anthracene, dimethyl anthracene, diphenyl hexatriene, diphenyl octatetraene, pyrene, and quatra phenyl. However, only a few dyes that we have examined survive without degradation at the high temperatures and relatively long residence times used for polymer processing. These are BOS, perylene, and BTBP. While all three dyes show the temperature effect in their spectra, we must point out that BTBP requires special care in this application because its Stokes shift is more sensitive to the polarity of the resin media than is the Stokes shift for perylene and BOS. As temperature increases, the changes in the polarity of the resin are seen as a shift in BTBP spectra in the blue direction.9 The effect is more prominent in polar glassy polymers such as polycarbonate, and for this reason we have chosen a polymer of low polarity, polypropylene, to demonstrate the temperature effect in BTBP. In our discussion below, we will limit the data analysis to that of perylene and BOS, but under limited circumstances the concepts also apply to BTBP.

DISCUSSION

There are various spectrum shape factors that one could use to calibrate the fluorescence spectra with temperature. We have chosen to use a ratio of intensities at



FIG. 5. Intensity vs. wavelength for BTBP doped into polypropylene for temperatures 132, 143, 154, 165, 175, 185, and 196 °C.



FIG. 6. Contour plot of correlation coefficient for ratio of intensities at all possible pair wavelengths vs. temperature for BOS doped into polycarbonate.

two wavelengths. By doing so, we not only avoid problems associated with absolute intensity measurements, but we also neutralize effects due to varying concentrations of dye in the matrix medium. The data of Figs. 3 and 4 are analyzed for the appropriate and optimum ratio of intensities by calculating all possible ratios of intensity across the full spectrum and correlating them with the overall temperature change. A statistics software package was used to develop all possible linear regressions of intensity ratios with temperature.

The results are presented as contour plots, as shown in Figs. 6 and 7. Here, wavelength is plotted vs. wavelength with contours that are labeled with the value of the correlation coefficient for a linear regression of intensity ratio vs. temperature. Each point of wavelength space represents the ratio of intensities at that wavelength pair, and its contour correlation coefficient value is a measure of the linearity of intensity ratio vs. temperature data. It is seen that there are several wavelength pairs for which the correlation coefficient approaches a value of one. Which of these to choose for the calibration function is deter-



FIG. 7. Contour plot of correlation coefficient for ratio of intensities at all possible pair wavelengths vs. temperature for perylene doped into polycarbonate.



FIG. 8. (a) Trough-to-peak intensity ratio vs. temperature for BOS doped into polycarbonate; (b) trough-to-peak intensity ratio vs. temperature for perylene doped into polycarbonate; and (c) trough-to-peak intensity ratio vs. temperature for BTBP doped into polypropylene. The relative uncertainty in the intensity ratio is 0.4%.

mined by the sensitivity or slope of the curve. For both BOS and perylene, the highest sensitivity is achieved by taking the ratio of intensities at the trough (464 for perylene and 422 for BOS) to that at the adjacent peak at longer wavelengths (476 for perylene and 434 for BOS). Trough-to-peak intensity ratios vs. temperature for BOS and perylene are shown in Fig. 8, where we have also added the trough-to-peak ratio for BTBP in polypropylene. Sensitivity of the trough-to-peak intensity ratio to temperature change is higher for perylene than for BOS. The data yield temperature sensitivity in the ratio of approximately 8.6×10^{-4} °C⁻¹ for BOS and 1.50×10^{-3} °C⁻¹ for perylene.

Although we have concentrated our analysis on linear correlations with temperature of the ratio of two intensities, there is no theoretical reason why this response should be linear; nor is there a rationale for choosing higher or lower order functions. Further analysis of the data is needed in order to determine whether other functions or other intensity relationships correlate with temperature and yield higher temperature sensitivity. If we polycarbonate/BOS



polycarbonate/perylene



FIG. 9. Sum-of-Gaussians fit to the fluorescence intensity vs. wavelength spectra at two different temperatures for BOS doped into polycarbonate.

consider the spectrum in terms of the model that is developed below, we would be inclined to integrate over wavelength regimes corresponding to spectral bands or inter-band regions and examine functions of the integrated spectral energy. For the practical application of this temperature measurement technique (to be described below) we use band pass filters to perform the integration. The use of band pass filters increases our signal-to-noise ratio, but sensitivity to temperature changes remains approximately the same.

A Phenomenological Model. Our initial step in the development of a model is to assume that the spectra of Figs. 3 and 4 can be described by a summation of intensity bands where each band has a Gaussian shape. To fit the spectra, we present a hypothetical fit to a spectrum of the form,

$$I(\lambda) = \sum_{i=1}^{n} a_i G_i(\lambda)$$
(1)

where I is fluorescence intensity, a is an amplitude factor, $G(\lambda)$ is a Gaussian function, and n is the number of Gaussian functions that are needed to fit the observed spectrum. Obviously, the Gaussian functions are centered on the peaks of the bands and in the vicinity of the shoulders of the spectrum at long wavelengths. To carry out the fit, approximate values of the Gaussian amplitudes, widths, and center wavelengths are assigned and then are permitted to assume their optimum value as a nonlinear

FIG. 10. Sum-of-Gaussians fit to the fluorescence intensity vs. wavelength spectra at two different temperatures for perylene doped into polycarbonate.

least-square fitting procedure is carried out. The results for the low and high temperature cases for BOS and perylene are shown in Figs. 9 and 10. The sum-of-Gaussians fit to the curves is excellent, and the figures display how fluorescence energy in the different bands changes with temperature. As temperature increases, we found that some of the Gaussian functions broaden a small amount; for example, the Gaussian for the first BOS band changes its width (σ of the Gaussian function) from 8.7 to 9.6 nm for the temperature change from 152 to 240 °C, while the widths of the other BOS bands change by less than 0.2 nm.

The decay scheme shown in Fig. 11 encapsulates the model concepts. The excited molecule dissipates energy via nonradiative or fluorescence decay with rate constants k and λ_{f} . The decrease in fluorescence intensity as temperature increases is the result of dissipation of energy through nonradiative decay paths depicted by the wavy lines with rate constants k_{i} . For perylene, nonradiative decay mechanisms can consist of molecular vibrations as well as intersystem crossing to an excited triplet state. BOS probably undergoes rotation about the central double bond upon excitation to the excited state, as well as intersystem crossing to the triplet state. For all cases, we assume that the probability of nonradiative decay is temperature dependent and can be expressed as a temperature activated rate function. Thus,

$$K_{\rm NR} = \sum_{i} k_{i} = \sum_{i} K_{oi} e^{-(\Delta H_{i}/RT)}$$
(2)



where K_{NR} is the rate of energy dissipated by nonradiative decay paths, K_{oi} is a pre-exponential constant, ΔH_i is the activation energy for the process *i*, *R* is the universal gas constant, and *T* is absolute temperature. There is a direct correspondence between decrease in fluorescence intensity and the increase in nonradiative energy dissipation. The change in fluorescence energy with temperature is a mirror image of changes in nonradiative decay so that as fluorescence decreases, nonradiative decay increases. We assume that temperature-dependent probabilities of decay to ground state energy levels via fluorescence are different for each fluorescence band and that temperature dependence can be expressed in terms of a thermally activated rate constant. Fluorescence intensity $I(\lambda, T)$ is expressed as

$$I(\lambda, T) = \left[\sum_{i} G_{i}(\lambda) A_{oi} e^{\Delta H_{i}/RT}\right] e^{-(h\nu/kT)}$$
(3)

where λ is the wavelength of light, $G_i(\lambda)$ is the Gaussian function of the *i*th band, A_{oi} is an amplitude for the *i*th band, *h* is Planck's constant, ν is the frequency of the light wave, and *k* is Boltzmann's constant. The quantity $\exp(-h\nu/kT)$ is the Boltzmann population factor, which has a negligible effect on the calculated intensity, less than 0.5% for the temperatures of our experiments.

Our ultimate objective is to use the temperature dependence of Eq. 3 to derive the linear calibration functions of Fig. 8. Equation 3 is used to calculate spectra using the observed spectra of Figs. 3 and 4 as a guide. In carrying out the calculation, we start with the sum-of-Gaussians fit to the data as obtained above. We assume the same temperature dependence for the width of Gaussian functions as was observed in Figs. 9 and 10. A non-linear least-squares fitting algorithm is invoked, varying ΔH_i and A_{oi} to obtain the best fit to the trough-to-peak calibration curves. Initially, a reasonable value of ΔH_i is chosen, recognizing that it is a molecular activation energy for a thermally activated process. The fit is undertaken within the confines of several constraints: the over-all decrease in spectral intensity with increasing temper-



FIG. 12. Calculated fluorescence intensity vs. wavelength and the calculated and measured trough-to-peak ratio vs. temperature for BOS doped into polycarbonate. The experimental data are the same as those of Fig. 8a.

ature is approximately a factor of two for both BOS and perylene; the ratio of intensities of the two larger peaks is fixed by the observations of Figs. 3 and 4; and the slope and intercept of the trough-to-peak ratio vs. temperature data are given by the linear fit to the data of Fig. 8. These constraints on the fitting process narrow the window of acceptable activation energies to values with relative variation of less than 10% and assure the uniqueness of the result. The calculated spectra and trough-topeak ratios for BOS and perylene are shown in Figs. 12 and 13.

Given that the trough-to-peak ratio is obtained from the data for the two shortest wavelength bands, its sensitivity to the fitting parameters is dominated by the values of ΔH and A_0 for those two bands. The values of ΔH for the two bands must be significantly different in order that the slope of the trough-to-peak ratio vs. temperature curve be greater than zero. For BOS, the fit yields ΔH_1 = 12.0 × 10³ J/mol and ΔH_2 = 15.2 × 10³ J/mol, and for perylene, ΔH_1 = 8.5 × 10³ J/mol and ΔH_2 = 17 × 10³ J/mol. These low values of activation energy imply that the path to nonradiative decay is easily traversed in the temperature range of these experiments. Also, a different activation energy for the individual bands means that fluorescence decay is described by multiple rates in the temperature range of our experiments.

Application to Polymer Processing. For application



FIG. 13. Calculated fluorescence intensity vs. wavelength and the calculated and measured trough-to-peak ratio vs. temperature for perylene doped into polycarbonate. The experimental data are the same as those of Fig. 8b.

of these concepts to polymer processing, we alter and simplify the experimental setup. Having identified the two dominant wavelengths that are to be used for the fluorescence temperature measurement, the experimental setup is changed from that of Fig. 2 to the arrangement shown in Fig. 14. Here, the monochromator is replaced by a beamsplitter that separates the fluorescence light into two beams that are detected by photomultiplier tubes (PMT) and are filtered at wavelengths λ_1 and λ_2 , the trough and peak wavelengths for the dye being used. The filters that we use for perylene are 5-nm band pass filters centered at 466 and 476 nm, and for BOS they are 5-nm filters centered at 422 and 433 nm. The 5-nm band pass of these filters allows for the significant enhancement in the intensity that we observe compared to that obtained from the monochromator. The relative uncertainty in the intensity measurements obtained with the beamsplitter/ PMT arrangement is in the range 0.07 to 0.2% for photon counts greater than 10⁶. In practice, however, the measurement uncertainty of concern to us is that for the trough-to-peak intensity ratio. This works to our advantage because effects due to fluctuations in the dye concentration and high voltage applied to the PMTs from a single power source are correlated and cancel out in the ratio. Thus, the dye acts as an internal standard that, for constant temperature, will yield the same ratio in spite of differences from sample to sample.



FIG. 14. The experimental arrangement used for monitoring polymer processing.

In fact, it is our experience that the uncertainty of the trough-to-peak ratio is often less than that observed in the individual intensities. Consider the data of Fig. 15. Here, we show the results of measuring the trough and peak intensities, I_1 and I_2 , from a specimen of polycarbonate doped with perylene. The measurements are from a linear scan over a length of 3 cm across the specimen and were obtained using the beamsplitter/filtered PMT detection scheme. The data, I_1 , I_2 , and I_1/I_2 , are plotted on equivalent scales to emphasize the difference in variations between absolute intensity measurements and the calculated ratio. The variations observed in I_1 and I_2 are due to variations in concentration of the dye as a function of position. The constant ratio I_1/I_2 reflects the fact that the specimen was maintained at a constant temperature, 21.3 °C. For these data, the relative uncertainties of I_1, I_2 , and I_1/I_2 are 2.2, 2.3, and 0.18%, respectively, i.e., the uncertainty for the ratio I_1/I_2 is an order of magnitude less than that for either I_1 or I_2 . Relative uncertainty in I_1/I_2 of 0.15% will yield temperature measurement uncertainties of 2 °C, a level of measurement uncertainty that we have achieved during polymer process monitoring.16

Process monitoring begins with obtaining a calibration curve using the beamsplitter/filtered PMT arrangement to measure a doped polymer in a temperature/pressure cell.



FIG. 15. The trough and peak intensities, I_1 and I_2 , and the ratio I_1/I_2 are shown for a linear scan across a specimen of polycarbonate doped with perylene.

Pressure effects must be taken into account because most polymer processing is carried out at elevated pressures. Although relatively small compared to thermal effects experienced during polymer processing, pressure effects are significant and a scheme to compensate for pressure is needed. To monitor polymer extrusion, we have used a linear compensation factor for pressures less than 40 MPa.¹⁶ A temperature calibration function with pressure compensation factor was used:

$$T = f\left(\frac{I_1}{I_2}\right) + CP \tag{4}$$

where I_1/I_2 is the ratio of the two measured fluorescence intensities, *P* is pressure, and *C* is a constant. Details of the application of Eq. 4 and measurements during polymer processing are published elsewhere.¹⁶

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