

# Fluorescence Based Temperature Measurements and Applications to Real-Time Polymer Processing

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We have used temperature sensitive fluorescent dyes, doped into polymer resins, to monitor the true resin temperature during extrusion processing. Two types of temperature sensitive fluorescent dyes were used: mobility dyes and fluorescence band definition dyes. When mixed with the resin at dopant concentrations, the fluorescent dye resides in a molecular neighborhood composed of resin molecules. Under these circumstances, its fluorescence spectrum reflects the resin temperature in its neighborhood. We apply this measurement concept to extrusion processing by using an optical sensor that accesses the machine at standard instrumentation ports. We show that, under processing conditions, the true resin temperature is significantly different from the machine temperature. Two examples of real-time process monitoring are presented: first, the effects of shear heating during extrusion were measured, and second, the effects of poor temperature control during extrusion were observed. The effects due to pressure on the fluorescence temperature measurements are examined. The fluorescence temperature measurements are compared to melt temperature thermocouple measurements.

## INTRODUCTION

Real-time temperature and pressure measurements of polymer resins have been the backbone of process monitoring for many years. For temperature measurements, both thermocouple and infrared radiometer transducers have been commercially available for insertion into standard instrumentation ports on processing machines. It is well known that experimental difficulties are experienced with both measurements (1–3). For example, when a melt thermocouple probe is positioned in the barrel of an extruder, the machine barrel temperature dominates its response because heat transfer from the barrel to the thermocouple junction is much more efficient than is heat transfer from resin to thermocouple. Phenomena such as shear heating and large temperature profiles in the resin flow stream are not seen because 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 such as with a filled resin.

The inadequacies of temperature measurements have major implications regarding rheological understanding of the process 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. The hardware of the measurement apparatus involves an optical fiber sensor that is inserted into existing instrumentation ports and is used to transmit excitation light to the resin and to collect the resultant fluorescence and transmit it to the detector (4, 5). Fluorescence is produced from a dye that is mixed with the resin at dopant concentrations, less than  $10^{-5}$  mass fraction of dye in the resin. 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 yields a true resin temperature.

Employing fluorescent dyes as temperature probes has been the subject of a number of studies (5–17). Both time resolved and steady state fluorescence measurements have been employed. Many researchers have used excimer producing fluorescent dyes, such as bis(pyrene) propane (BPP), for which intramolecular rotational motion is the basis of the dye's temperature response (5, 8, 10, 11, 14, 16, 17). For the most part, published work is not concerned with measuring temperatures in polymers nor is it concerned with the high temperature ranges used for polymer processing. We have used BPP to monitor polymer injection molding and to measure temperature gradients in an extruded flow stream (4, 5). But, BPP is somewhat limited in

application because it is susceptible to photobleaching and because it degrades at temperatures above 220°C. Many polymer processes are carried out at temperatures higher than 220°C, and because of this we have embarked on a search for fluorescent probes that can be used up to 300°C. During the course of this search we identified a new class of temperature sensitive dye that we call fluorescent band definition dyes (18). In contrast to the mobility based photochromic activity of excimer producing dyes, temperature sensitivity of band definition dyes is quantum mechanical in origin. In this paper we will describe the performance and application of two band definition dyes, benzoxazolyl stilbene (BOS) and perylene, and also, we present work that we have done using BPP to monitor polymer extrusion.

Given that polymer processing is usually done at elevated pressure, the effects due to pressure on fluorescence temperature measurements need to be considered. Below, we will discuss the use of a pressure compensation factor in the calibration function for temperature measurements.

### EXPERIMENTAL PROCEDURE

Fluorescent dyes for process monitoring are chosen using these criteria: 1) they must survive the high temperature 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 we have used for high temperature processing applications are shown in Fig. 1. The excimer producing dye BPP was obtained from Molecular Probes Inc., and band definition dyes, perylene and benzoxazolyl stilbene (BOS), were obtained from Aldrich Chemicals (19). The excitation wavelength for bis-pyrene propane is 345 nm with monomer fluorescence extending from 360 nm to 440 nm and excimer fluorescence from 460 nm to 560 nm, for perylene excitation is at 410 nm with fluorescence from 430 nm to 530 nm, and for BOS excitation is 365 nm with fluorescence extending from 390 nm to 470 nm. We have used perylene and BOS up to 300°C without observing degradation, but BPP is limited to temperatures below 220°C.

Two resins were used for these studies: poly(methyl methacrylate) (Carboset 1034 from Union Carbide) and polycarbonate (Dow Chemical 200) (19). Dye doping was carried out by first dissolving the dye in solution, pouring this solution over 5% of the to-be-processed resin pellets, evaporating the solvent leaving behind

pellets coated with dye. The coated pellets were then mixed with the 95% uncoated pellets. During extrusion processing, pellets were brought to the melt state and blended together in an extruder or conveying screw line that mixed the dye throughout the batch. The mixing is not uniform, but the effects of variations in concentration are eliminated from our fluorescence measurement by expressing the data as a ratio of fluorescence intensities at two different wavelengths.

In order to establish the details of temperature sensitivity, spectra as a function of temperature and pressure were obtained using temperature controlled pressure vessels based on designs described by Migler and by Weber (20, 21). A typical setup is shown in Fig. 2 where the measured specimen is in a temperature controlled pressure cell, oven or processing machine. The primary modules of the measurement apparatus are: a light source that is either a laser or a xenon arc lamp, a bifurcated optical fiber cable, the optical sensor, and a light detector consisting of a monochromator with CCD detector or a dichroic mirror beamsplitter (for separating spectra into different wavelength regimes) with filtered photomultiplier tube (PMT) detectors. The bifurcated optical fiber cable consists of a bundle of 100  $\mu\text{m}$  core fibers, half of which carry excitation light to the resin, and half of which transmit fluorescence to the detector. For obtaining detailed spectra, the optical signal is sent to a monochromator. In order to maximize the rate of

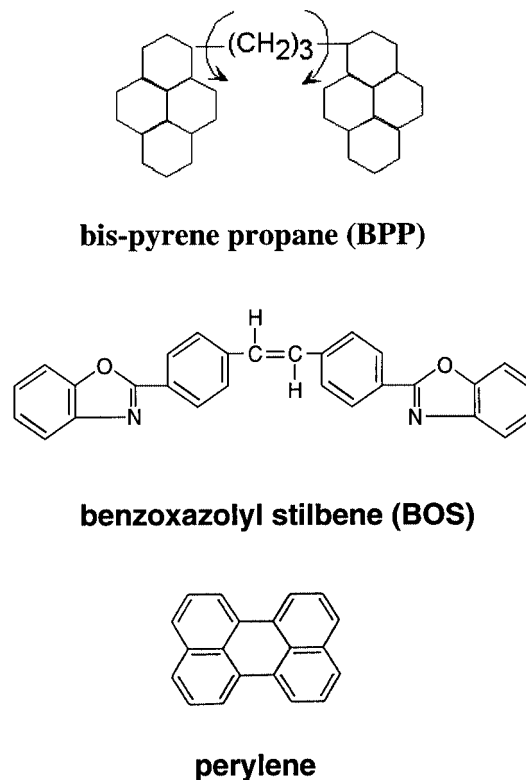


Fig. 1. The molecular structures of three fluorescent dyes for polymer processing are shown.

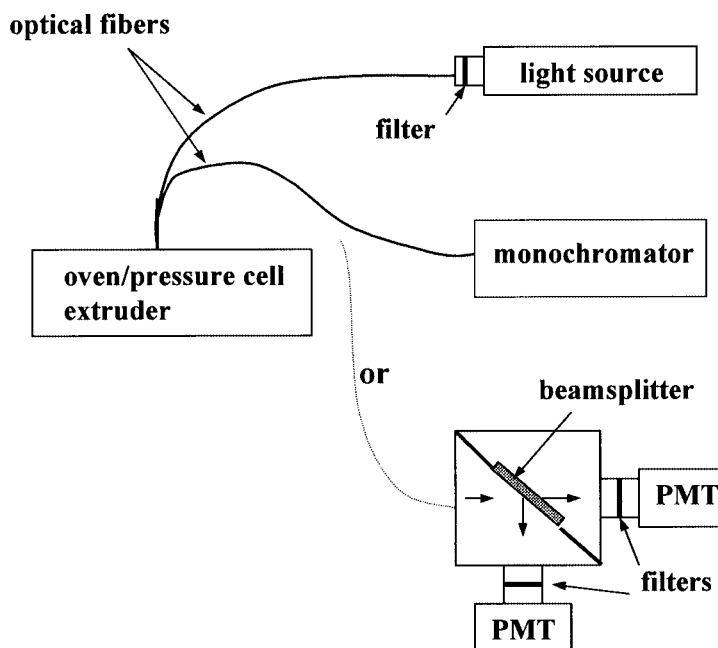


Fig. 2. The experimental setup using the optical fiber sensor is shown. Alternate detector arrangements are the monochromator and the beamsplitter with filters.

data acquisition during process monitoring, however, only the intensities at two wavelengths are monitored. This is accomplished by splitting the optical signal with a beamsplitter and filtering the two separated intensities with specific band pass filters. For perylene, 5 nm band pass filters centered at 464 nm and 473 nm were used; for BOS, 10 nm bandpass filters centered at 420 nm and 436 nm were used; and for BPP, a 10 nm bandpass filter centered at 400 nm and a 40 nm bandpass filter centered at 500 nm were used. In each case the bandpass filters were chosen in accordance with the temperature/pressure dependencies observed in the full spectrum for each dye. Representative spectra are shown below, but full details of fluorescence spectra for these dyes as a function of temperature and pressure and the analysis of these data will be published in a separate paper (22).

Sensor access to the processing machine is achieved through an existing instrumentation port. For extruders, this is the standard 1/2 inch diameter sensor port normally used for temperature and pressure transducers. For injection molding machines, we have constructed a sensor that substitutes for an ejector pin consisting of a sleeved rod with a sapphire window at its end (4). A 1/2 inch diameter bolt with optical fiber is depicted in Fig. 3. An advanced design of this sensor contains a focusing lens and has confocal optics geometry (5, 18).

For one of the applications described below, we use a slit die rheometer that is attached to a single screw extruder. The rheometer, based on a design by Springer, contains standard 1/2 inch ports that receive our optical sensor bolt (23).

## RESULTS AND DISCUSSION

**Temperature Sensitive Fluorescent Dyes.** In Fig. 1, the arrows indicate flexibility in the BPP molecule about the propyl alkane linkage between the two pyrene rings. This flexibility allows the creation of an excimer state that occurs when the two pyrene rings rotate into a position of close molecular contact (24–26). When one of the pyrene rings absorbs excitation energy at 345 nm, it decays to its ground state either by a radiative monomer transition with fluorescence intensity  $I_m$  having maxima at 380 and 400 nm, or by radiative excimer transition  $I_{ex}$  in the range 460 nm to 560 nm that occurs when an excited pyrene ring comes in close molecular contact with its unexcited neighbor. The probability that an excited pyrene ring can rotate to the excimer position before its own fluorescence decay occurs is dependent on  $\tau_r$ , the intramolecular rotational relaxation time.  $\tau_r$ , in turn, depends on the ratio of viscosity  $\eta$  to temperature  $T$  in its molecular neighborhood,

$$\tau_r = A \frac{\eta}{T} \quad (1)$$

where  $A$  is a constant of proportionality. At constant pressure, the ratio  $I_{ex}/I_m$  increases with increasing temperature because lower viscosity at high temperatures produces a shorter  $\tau_r$  and permits increased excimer state formation (17).

Pressure dependence enters through the viscosity and can be expressed as

$$\eta = \eta_0 e^{\frac{\Delta E}{RT}} e^{\alpha P}. \quad (2)$$

Here,  $E$  is activation energy,  $R$  the gas constant, and  $\alpha$  is a pressure factor. Thus, for a mobility dye,

temperature and pressure effects are phenomenologically entangled through Eq 2. This implies that temperature measurements will require pressure compensation.

A temperature calibration function containing a pressure compensation factor is expressed as

$$T = F(I_{ex}/I_m) + CP + DP^2, T > 140 \text{ (}^\circ\text{C)} \quad (3)$$

where  $F(I_{ex}/I_m)$  is the functional fit to the temperature versus  $I_{ex}/I_m$  calibration curve obtained at atmospheric pressure, P is pressure. C and D are the pressure compensation constants that were obtained by calibration in a pressure controlled cell. For BPP doped into PMMA, we obtained  $C = 0.44 \text{ }^\circ\text{C}/\text{MPa}$ ,  $D = 0$  and

$$\frac{I_{ex}}{I_m} = 2.51 \times 10^{-5}T^2 - 6.13 \times 10^{-3}T + 0.385 \quad (4)$$

where T is expressed in  $^\circ\text{C}$  and P in MPa. The standard uncertainty in the measurement of  $I_{ex}/I_m$  is 0.2%, and the uncertainty in the coefficient C is  $0.01^\circ\text{C}/\text{MPa}$ . Eq 4 is derived from the data of Fig. 4

that show the change in the ratio  $I_{ex}/I_m$  as a function of temperature at atmospheric pressure. It should be understood that the coefficients in Eq 4 hold only for the experimental setup that was used to obtain them. This is because the transmission factors of the filters and the amplification factors of the particular PMTs used in the calibration experiments are inherent in the coefficients of Eq 4. (This is also true for Eq 5 below.)

In contrast to mobility dyes, temperature/pressure effects seen in the spectra of band definition dyes are quantum mechanical in origin (27). Temperature and pressure induced changes in the spectra are due to changes in ground state and excited state energy levels and to transition probabilities of decay to different energy bands in the ground state. Consider the spectra for perylene in polycarbonate shown in Fig. 5. Distinct bands, seen at 452 nm and 473 nm, are associated with 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 at energy levels associated with decay at 452 nm and 476 nm as depicted in Fig. 5.

Fig. 4. The calibration curve,  $I_{ex}/I_m$  versus temperature at atmospheric pressure, is shown for BPP doped into PMMA. The equation is a quadratic fit to the data.

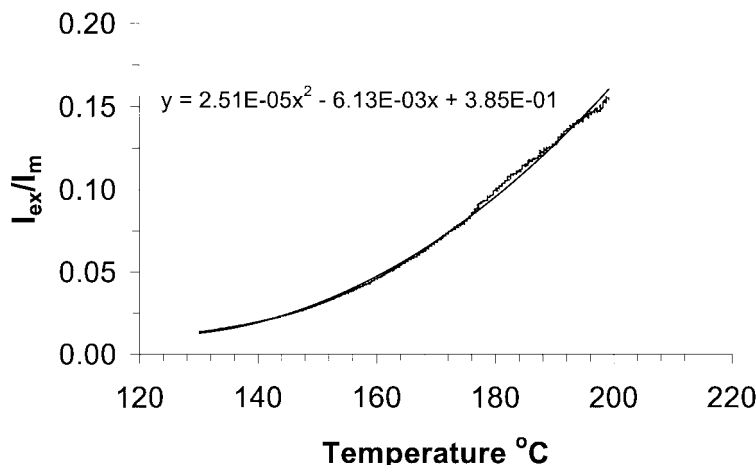


Fig. 5. Fluorescence spectra for polycarbonate doped with perylene are shown for a series of temperatures ranging from 180°C to 295°C. Data were obtained at atmospheric pressure.

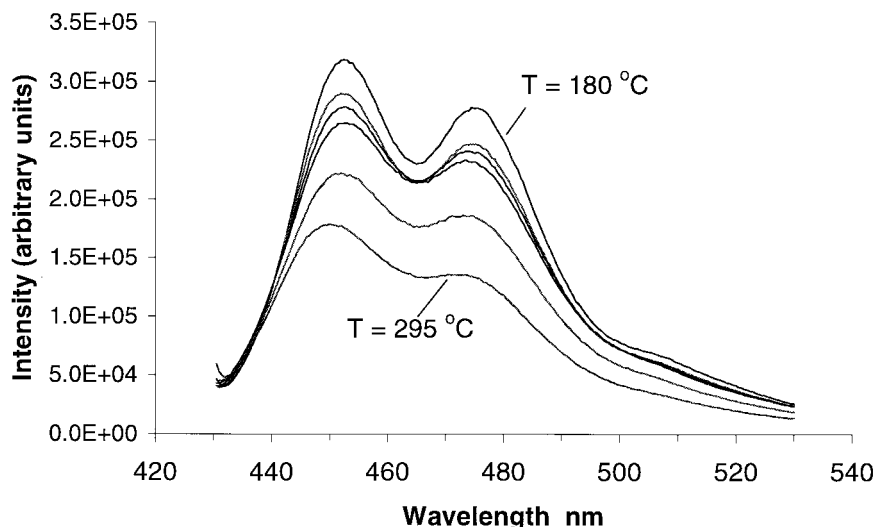


Fig. 6. The calibration curve,  $I_{464}/I_{473}$  versus temperature at atmospheric pressure, is shown for perylene doped into polycarbonate.

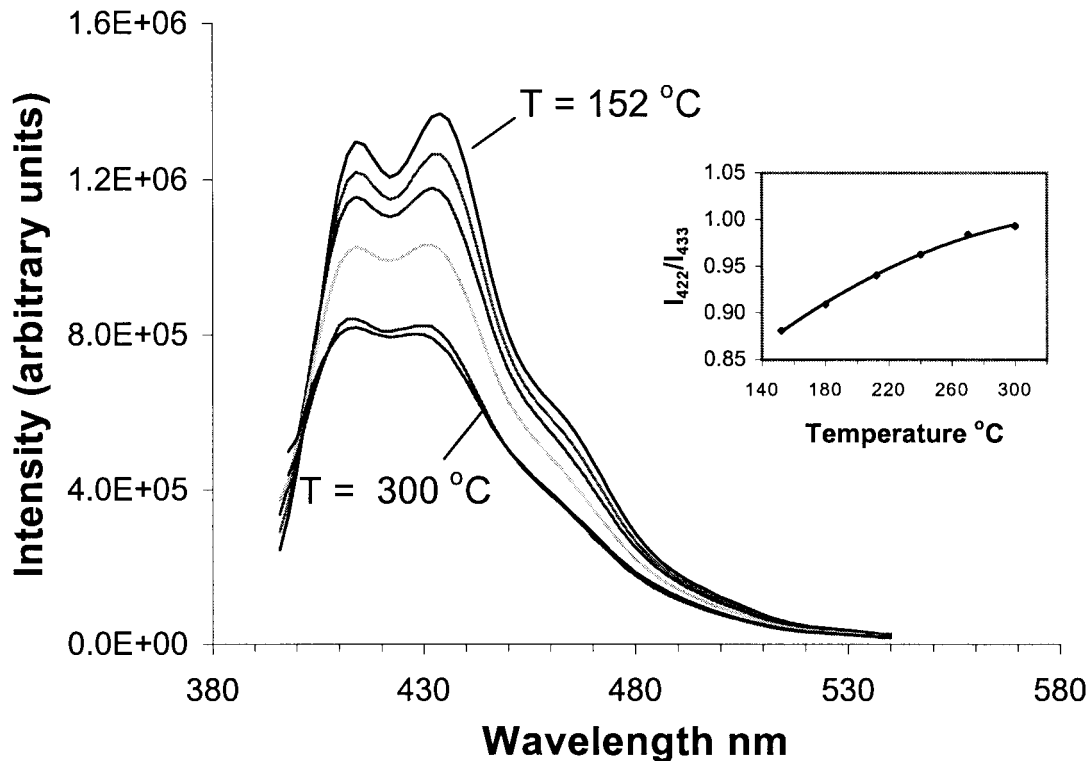
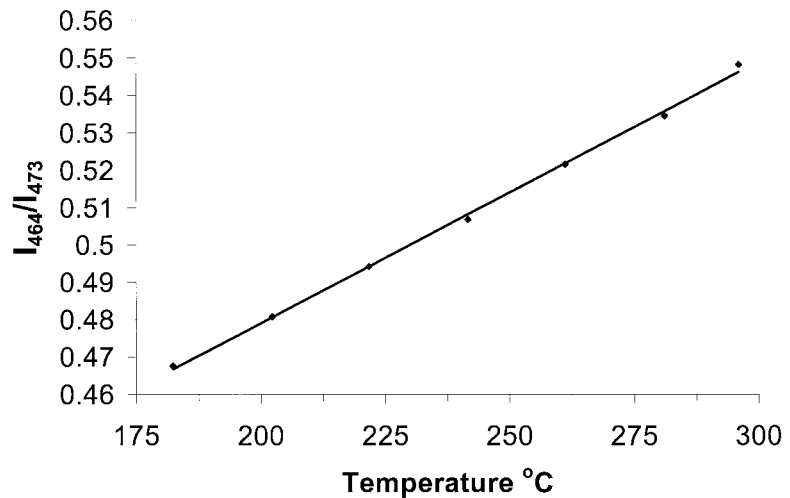


Fig. 7. Fluorescence spectra for polycarbonate doped with BOS are shown for a series of temperatures ranging from 152°C to 300°C. Data were obtained at atmospheric pressure. The inset is a calibration curve of  $I_{422}/I_{433}$  versus temperature.

The basis of the temperature sensitivity of the fluorescence decay is the temperature 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 the 452 nm and 473 nm peaks as temperature increases.

The temperature measurement is based on the calibration curve of Fig. 6 where we have plotted the ratio  $I_{464}/I_{473}$  versus temperature for atmospheric pres-

sure. When the pressure compensation factor is added, the calibration function becomes

$$T = 1.432 \times 10^3 \frac{I_{464}}{I_{473}} - 485.7 + 2.16P \quad (5)$$

where T and P have units of °C and MPa. The standard uncertainty in the measurement of  $I_{464}/I_{473}$  is 0.3%, and for the pressure measurements it is 0.03 MPa. The standard uncertainty in the thermocouple measurement used for obtaining the calibration func-

tions of Eq's 4 and 5 is 0.5°C. Eqs 4 and 5 hold for pressures up to 26 MPa. Obviously, accurate temperature measurements require simultaneous acquisition of pressure; a measurement normally carried out during polymer processing. The highest pressure experienced in the extrusion experiments described below was 20 MPa.

Spectra at atmospheric pressure for BOS doped into polycarbonate are shown in Fig. 7. The similarity between the perylene and BOS spectra and their temperature dependence is obvious. A calibration curve

for the BOS data is shown as an insert in Fig. 7. With the data of Figs. 5 and 7, we demonstrate the generality of the band definition phenomenon. It is observed in many dyes, but only a few can be used at high processing temperatures used for polymer processing. The temperature measurement sensitivity for perylene and BOS as established from the data of Figs. 5 and 7 is equivalent, both yielding sensitivity in the ratio of intensities of approximately  $2 \times 10^{-3} \text{°C}^{-1}$ . Thus, results from processing applications using only one of these dyes, perylene, is presented below.

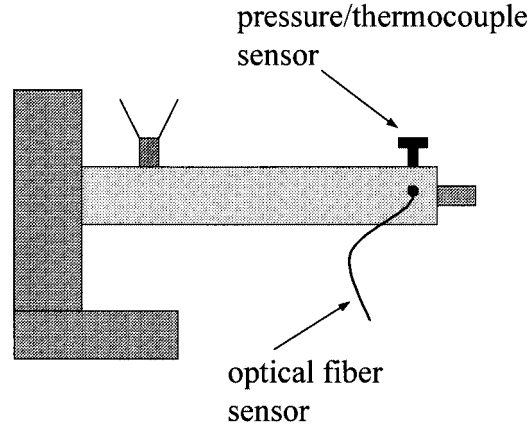


Fig. 8. The position of sensors on the extruder for the data presented in Figs. 9 and 10 is shown.

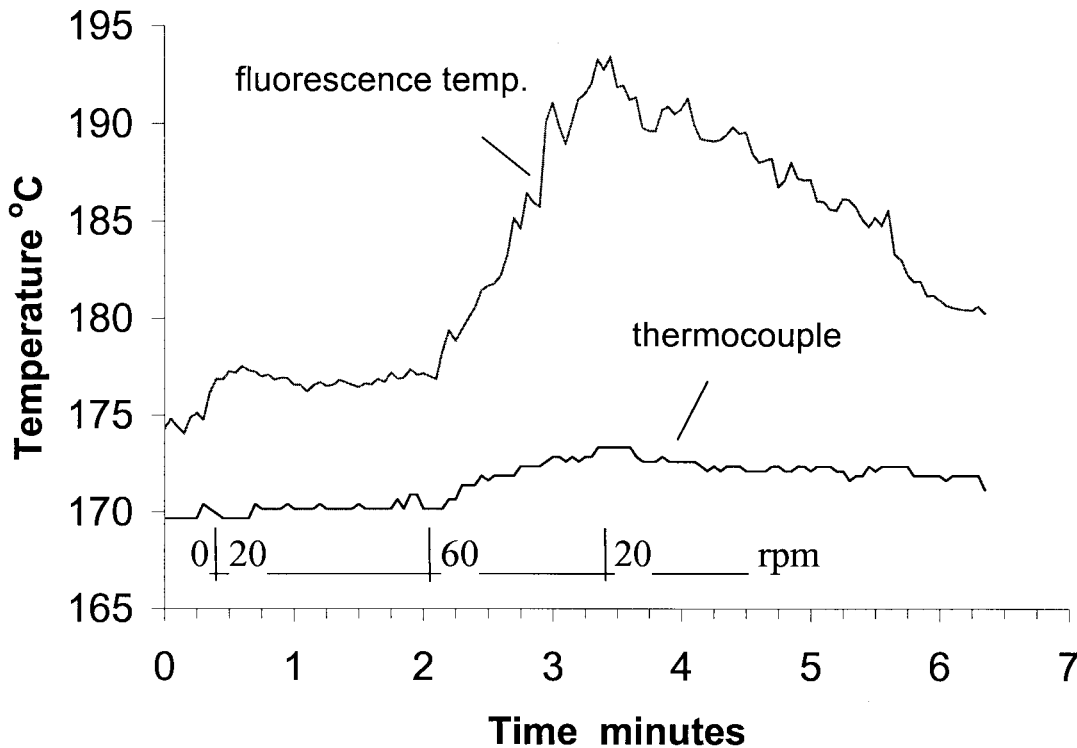


Fig. 9. Fluorescence temperature and barrel thermocouple temperature for extrusion of PMMA doped with BPP are plotted versus time. Screw rpm is indicated.

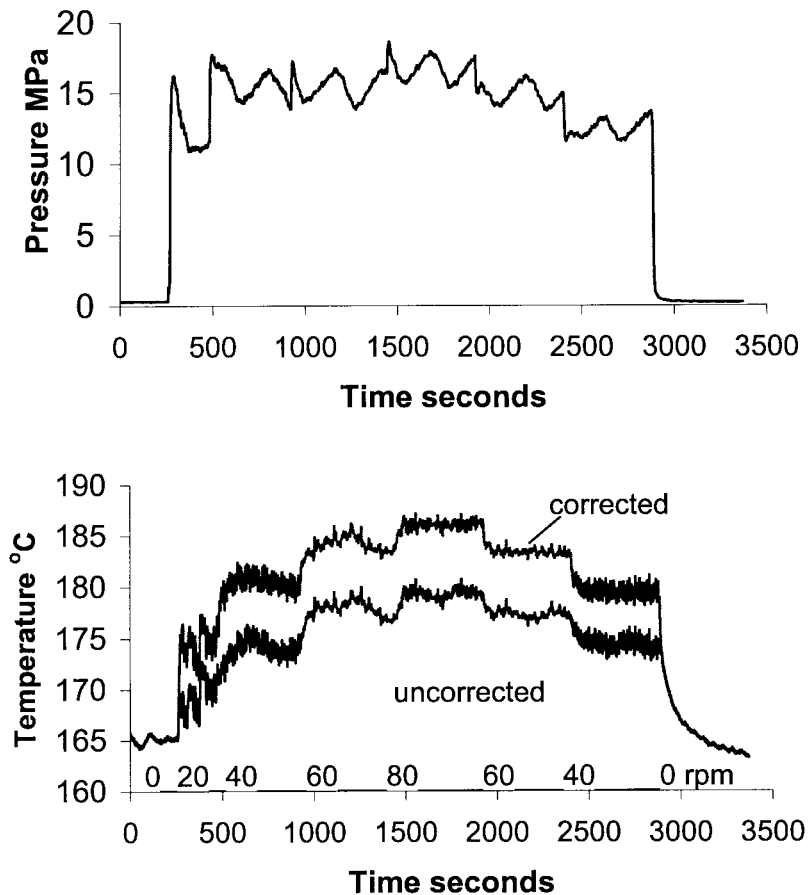


Fig. 10. Pressure and fluorescence temperature versus time are plotted for PMMA doped with BPP. The corrected temperatures have been calculated using the pressure compensation factor shown in Eq 4 along with the measured pressures. The uncorrected data have not been pressure compensated.

A fundamental question arises concerning the measurement method: What is the effect of shear on the temperature measurement? The question is appropriate because calibration curves were obtained at quiescent conditions. We have addressed this question using fluorescence anisotropy measurements during shear flow (28). Measurements on perylene doped into polyethylene show that isotropic orientation of the perylene molecule is maintained for shear rates from  $0 \text{ s}^{-1}$  to  $100 \text{ s}^{-1}$ . This means that the perylene dye occupies microscopic free volume regions in the resin and is not oriented by the shear stresses that are supported by the macromolecular entanglement structure of the polymer. At high shear rates the local molecular environment presents itself to the perylene molecule as though it was in the quiescent state. Fluorescence anisotropy of BPP has not been measured during shear flow, but for the application presented below the sensor was placed in the extruder barrel beyond the end of the screw, a region of low shear rate flow.

**Application to Polymer Processing.** The results of two experiments are reported here. First, real-time measurements of temperature during extrusion of Carboset PMMA doped with BPP are presented for the purpose of demonstrating shear heating effects. Second, we use perylene to monitor the temperature of polycarbonate extruded through a slit die rheome-

ter. Using the mobility dye BPP, we achieve a lower temperature measurement uncertainty than is possible with the band definition dyes. BPP is the dye of choice for applications when the temperature does not exceed its degradation threshold,  $220^\circ\text{C}$ . For processing polycarbonate, however, either perylene or BOS must be used because processing is normally carried out in the range  $260^\circ\text{C}$  to  $290^\circ\text{C}$ .

Extrusion of Carboset PMMA doped with BPP was monitored with the setup shown in Fig. 8. An optical fiber sensor and a combination thermocouple/pressure transducer were inserted in instrumentation ports at the same axial position near the end of a single screw extruder barrel. The results are shown in Fig. 9, where we have plotted thermocouple and fluorescence temperature versus time. With the barrel set-point temperature at  $170^\circ\text{C}$ , measurements were initiated in the quiescent state whereupon screw revolutions per minute (rpm) were increased in steps to 20, 60 and back to 20 rpm. Using Eq 4, temperature was calculated from the measured  $I_{\text{ex}}/I_{\text{m}}$  ratio. At 60 rpm, we observed the fluorescence temperature to increase  $20^\circ\text{C}$  above the initial temperature, but the thermocouple temperature increased by only  $3^\circ\text{C}$ . The fluorescence temperature is an average of the true resin temperature within the view of the optical sensor, whereas the thermocouple reading is dominated by

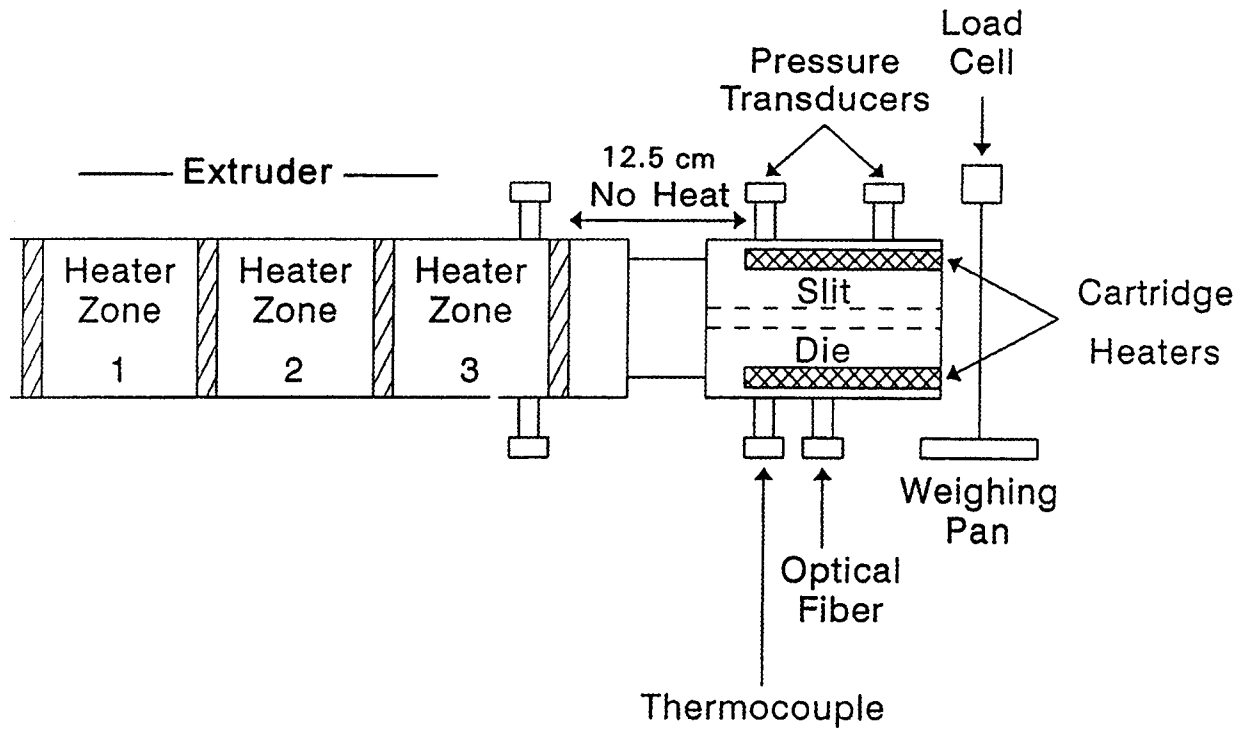


Fig. 11. The experimental setup using a slit die at the exit of the extruder is shown. The region without temperature control is indicated. Data of Fig. 12 and 13 were obtained from the slit die sensors.

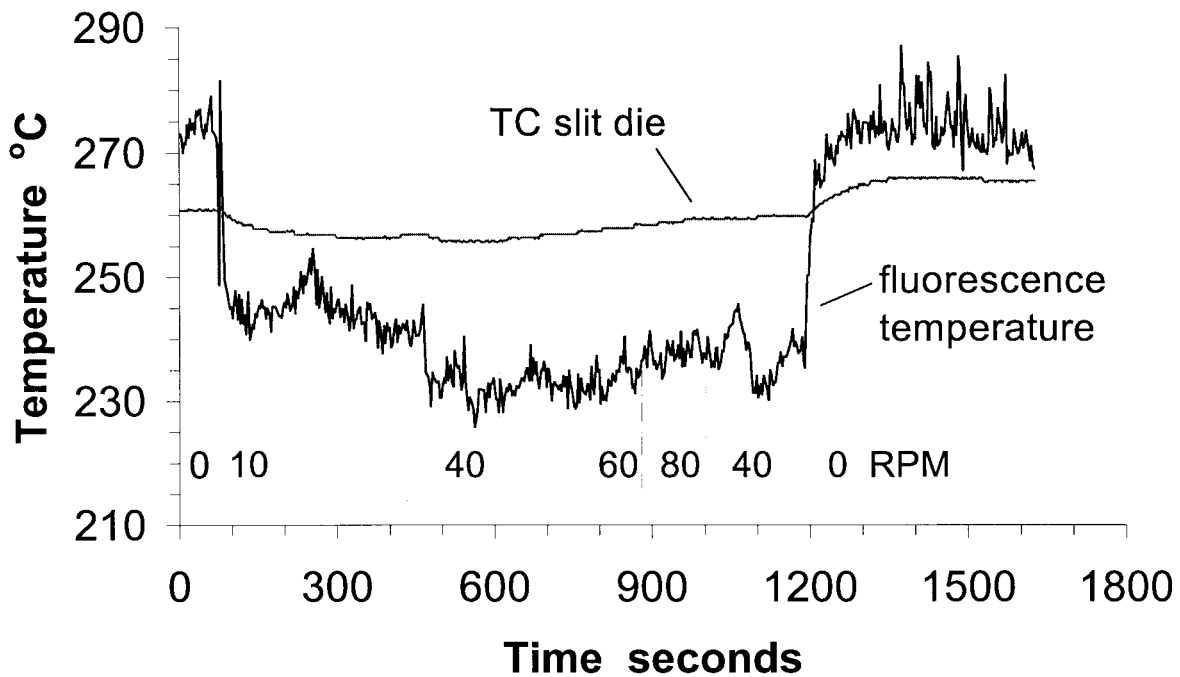


Fig. 12. Temperature versus time is shown for extruded polycarbonate doped with perylene. The fluorescence and the thermocouple (TC) temperatures were obtained from the sensors in the slit die of Fig. 11. Screw rpm is indicated.



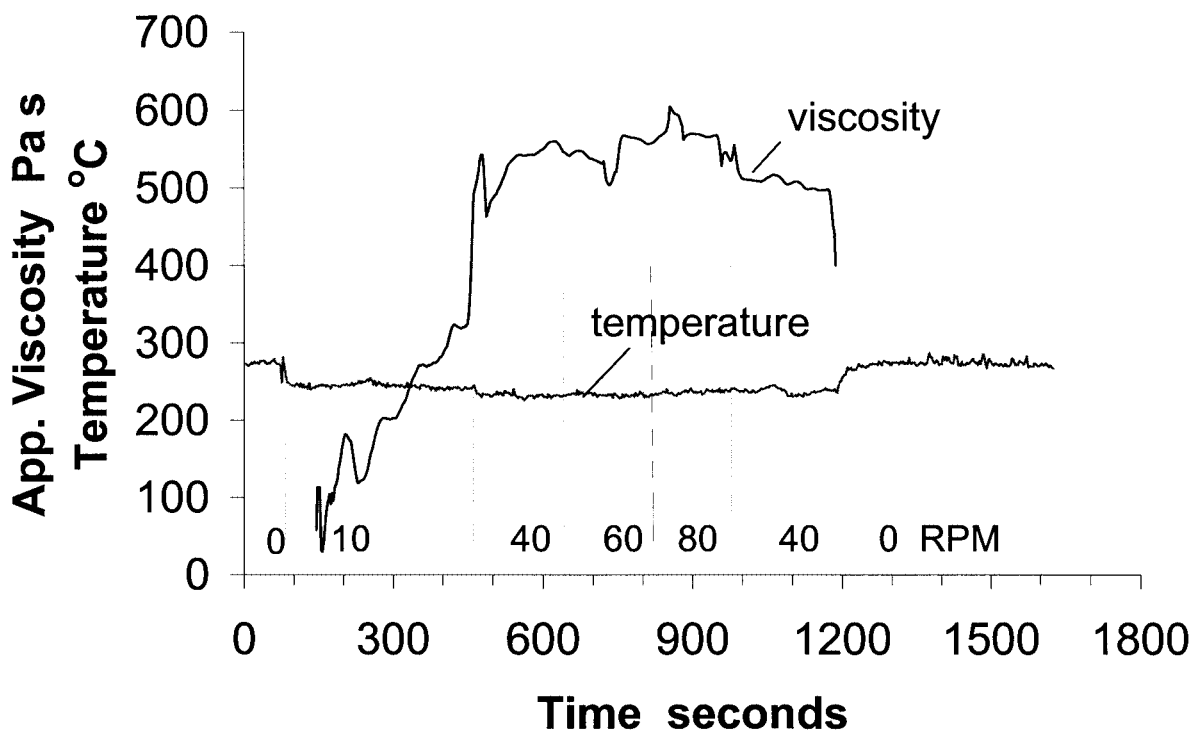


Fig. 13. Apparent viscosity and temperature are plotted versus time for extruded polycarbonate doped with perylene. The fluorescence temperatures are the same data as shown in Fig. 12. Screw rpm is indicated.

the large thermal mass of the extruder machine and reflects barrel temperature rather than resin temperature. These measurements show the large effect due to shear heating on the resin temperature, and demonstrate that it is not possible to accurately assess this effect using the standard barrel thermocouple. The standard uncertainty in the fluorescence temperature is 1.5°C and for the thermocouple reading it is estimated to be 0.5°C.

The magnitude of the pressure compensation in these measurements is shown in Fig. 10. Here, pressure and fluorescence results are shown for an extrusion of PMMA for which screw speed is ramped from 0 rpm to 80 rpm returning again to 0 rpm. Both compensated and uncompensated temperature results are shown. The corrected (pressure compensated) results were obtained by utilizing Eq 4 and the real-time pressure measurements in point-by-point correction of the uncorrected data. At 80 rpm the pressure compensation corrects the temperature value by approximately 7°C. The standard uncertainty in the corrected temperature measurement is 1.5°C and for the pressure measurements it is 0.03 MPa.

Fig. 11 illustrates the setup for a single screw extruder instrumented with a slit die rheometer at the exit. Three heater bands control barrel temperature, and the slit die temperature is controlled using four cartridge heaters. For the data presented in Fig. 12, the transition region, extending over 12.5 cm between barrel and slit die, was unheated. We processed polycarbonate doped with perylene and monitored the temperature at the midsection of the slit die where

the optical sensor was located. The thermocouple in the slit die, which is situated adjacent to the unheated region, was used to control slit die temperature at 265°C. Heat loss from this thermocouple position into the unheated region caused the controller to deliver excess heat. At 0 rpm, evidence of excess heating was seen as an elevated resin temperature, approximately 280°C or 15°C above the set point, which was calculated from the measured ratio  $I_{464}/I_{473}$ . As screw rpm increased, resin from the unheated region was pushed into the slit die causing a rapid decrease in temperature to 230°C. At 80 rpm, the slight increase in temperature can be attributed to shear heating. When the extruder was turned off resin temperature quickly increased to 280°C. The fluctuations in the temperature data are significant and are considered to be a true reflection of the temperature gradients in the flowing resin. During this process, temperature measured by the control thermocouple decreased by approximately 5°C and returned to the set point when extruder operation ceased. The standard uncertainty of fluorescence temperature measurements using perylene is 2.5°C.

One effect of inadequate thermal control of the process is on the rheology of the flow stream such that resin viscosity increased sharply in the uncontrolled region. The apparent viscosity, calculated from the slit die dimensions, the pressure drop and volume flow rate measurements, is shown in Fig. 13 (23). Although shear rate is increasing during the course of this run, a corresponding shear thinning decrease in viscosity is not seen because the large decrease in

temperature dominates the viscosity changes. The data illustrate the need to have accurate temperature control along the full length of the extruder. The standard uncertainty in the viscosity measurements is 6%.

In conclusion, we have demonstrated the application of fluorescence thermometry using two types of fluorescent dyes, a mobility dye (BPP) and a fluorescence band definition dye (perylene). The fluorescent band definition dyes are a new class of dye that can be employed in high temperature processing applications. The temperature responses of perylene and BOS were examined by doping them into polycarbonate and observing changes in their fluorescence spectra over a range of temperatures extending from 180°C to 300°C. We have shown that a melt thermocouple flush mounted in an extruder barrel yields temperature measurements that are significantly different than the true resin temperature as measured by the fluorescence method. Heat generated by shearing forces in combination with the insulating character of polymer resins causes large increases in temperature that can approach the degradation temperature. Also, we have demonstrated the importance of maintaining good temperature control along the full length of the extrusion line.

An objective of our continuing study of pressure and temperature induced changes in band definition dyes is to separate the two effects. It is not possible to do so in all cases, but we have found that, for BOS doped into polystyrene, pressure and temperature produce different changes in the spectra. For this case, we hypothesize that temperature determines the population of each energy level thus affecting the fluorescence intensity of each band, and pressure produces a perturbation in the energy level that is reflected in a wavelength shift in the spectrum. These phenomena are the basis for separating temperature and pressure, leading to a fluorescence based temperature measurement that does not require pressure compensation. This topic will be discussed in a future publication (22).

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