An Easy Method To Monitor Lactide Polymerization with a Boron Fluorescent Probe

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ABSTRACT Fluorescence spectroscopy has been widely used to monitor different polymer processes such as polymerization kinetics, chain entanglements, and thermal transitions. The solvent-free controlled ring-opening polymerization (ROP) of lactide is significant both commercially and for research; thus, monitoring this process with a simple fluorescence method can be very useful. Here, a fluorescent dye, difluoroboron 4-methoxydibenzoylmethane (BF_2dbmOMe) is employed to probe lactide bulk ROP by measuring the emission from solidified reaction aliquots at room temperature. It was found that, through the course of polymerization, the fluorescence of BF_2dbmOMe in the solid-state aliquots exhibited a systematic shift from yellow to green and then to blue, accompanied by a gradual reduction in the decay lifetime. The fluorescence color change is sensitive to the monomer percent conversion, not the polymer molecular weight. On the basis of these observations and experimental data, we propose that the long-wavelength emission with perceivably longer lifetimes arises from BF_2dbmOMe dye aggregates (ground and/or excited states), while the dissolved individual dye molecules are responsible for the blue fluorescence with a shorter lifetime. This demonstration of the utility of BF_2dbmOMe as a fluorescent probe for lactide polymerization could have important practical implications.

KEYWORDS: polylactide • ring-opening polymerization • fluorescence spectroscopy

INTRODUCTION

Fluorescent molecules have been used to monitor polymer structure, properties, and processes because of their easy implementation and high sensitivity (1). Examples include polymerization kinetics (2, 3), microenvironments (4, 5), chain mobility (6, 7) and entanglements (8, 9), thermal (10) and phase (11, 12) transitions, mechanical stresses (13), aging (14, 15), degradation (16, 17), and sol−gel reactions (18, 19). The use of fluorescence spectroscopy to study in situ polymerization kinetics, one of the most important processes in polymer chemistry, is often based on changes in the fluorescence quantum yield, lifetime, or emission color (1). Although the optical properties of these fluorescent dyes are almost solely dependent upon the viscosity/rigidity of the system, the probing mechanisms, vary significantly. For example, some dye probes are prone to thermal quenching in more fluid environments (e.g., liquid monomers), but their fluorescence quantum yield may be dramatically enhanced when the surroundings become viscous enough to disrupt the bond rotations and vibrations (20). For some other probes with intramolecular charge-transfer transitions (21), the increase in the substrate rigidity can inhibit this charge-transfer process, which typically requires some molecular rotation to form a twisted geometry in the excited state (2). Because the twisted structure is a more stable excited-state conformation, a hypsochromic shift (increase in energy) in the emission is often observed with polymerization. Finally, some planar, polyaromatic hydrocarbons (PAHs) such as pyrene form excited-state dimers (excimers) in organic solvents. Because the excimer formation rate is diffusion-controlled (22, 23), more viscous polymers (e.g., with a higher molecular weight) are likely to suppress the excimer emission (24). Thus, a ratiometric method based on monomer/excimer emissions of these PAHs could also be devised to report polymerization processes. A large variety of molecules exhibit rigidochromic photoluminescence (25) and serve as good candidates for polymer probes. The substrates, however, are usually acrylic or styrene systems, given the important industrial applications of these polymers (26). Furthermore, the progressive viscosity increase from liquid to solid during polymerization provides a relatively easy platform to apply rigidochromic fluorescence-based probes.

Recently, with green chemistry and sustainability gaining increased public attention (27), bioderived and biodegradable poly(lactic acid) (PLA) (28) is becoming widely used in many fields, from cutting-edge research of bioengineering and biomedical research (29) to everyday use as thermal plastics (30) and food-packaging (31) materials. PLA can be produced either by stepwise polymerization of lactic acid from crop fermentation or by ring-opening polymerization (ROP) of lactide (32), the dimer of lactic acid. The former generally results in low-molecular-weight (low-MW) PLA with a broad polydispersity index, which significantly limits its

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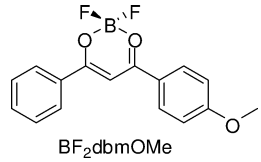
applications, while lactide ROP gives well-defined PLA with MWs up to 10^6 Da (33). Industrial production of PLA via lactide ROP is normally solvent-free, with an alcohol as the initiator and a metal complex [such as tin(II) 2-ethylhexanoate, $Sn(oct)_2$] as the catalyst. Under these conditions, fluorescent probes that rely on a rigidity change may still function at typical reaction temperatures (above the melting point of lactide crystals). At room temperature, however, where optical measurements are usually performed, the samples solidify and the extent of reaction may not be easily probed by rigidochromic fluorescent dyes.



BF_2dbmOMe

Here, we report that a simple boron diketone complex, BF_2dbmOMe, can be used as a fluorescent probe for solvent-free lactide ROP and allows for sample measurement in the solid state at room temperature. Previously, it was found that BF_2dbm derivatives exhibit tunable fluorescence (34), room-temperature phosphorescence (RTP), and delayed fluorescence (35, 36). Importantly, their multiemissive properties are very sensitive to the microenvironments in which the dye resides (37, 38). For example, polymer conjugates BF_2dbm−poly(ϵ-caprolactone) (BF_2dbmPCL) (38) and BF_2-dbmPLA (35) are chemically similar polyesters, but BF_2dbmPCL is non-phosphorescent at room temperature, while BF_2dbmPLA has visible green RTP under nitrogen. This observation has been attributed to the differences in the solid-state polymer properties of PCL and PLA (e.g., glass transition temperature, T_g, and free volume, V_f). It was proposed that more crystalline materials such as PCL tend to exclude the boron dye from ordered regions, whereas the dye distributes rather evenly in amorphous PLA. Also, because PCL has a much lower T_g (−60 °C) than PLA (∼60 °C), the boron dye likely possesses more rotational and vibrational freedom in PCL than in PLA, thus efficiently quenching its RTP in PCL intercrystalline regions (37, 38). In the case of lactide ROP, the starting monomer is crystalline too, but the final product PLA is glassy at room temperature. As ROP proceeds, more amorphous, glassy polymer is produced. Because BF_2dbmOMe fluoresces differently in amorphous versus crystalline substrates, it could be a good probe of lactide polymerization too.

Another reason that BF_2dbmOMe may be suitable for such an application is because both its aggregate (ground and excited states) and monomer forms are highly fluorescent with distinctly different emission wavelengths and lifetimes. Its emission profile in the solid, aggregate state is relatively uncomplicated compared to other boron dyes that form different polymorphs displaying different emission colors (39, 40). BF_2dbmOMe exhibits yellow fluorescence regardless of the solid form and processing conditions. Furthermore, this dye resembles the polymerization initiator, BF_2dbmOH, used to make dye−polymer conjugates, the optical properties of which have been the focus of numerous studies. Because the boron dye is less likely to be embedded in the tightly packed lactide crystals than the porous PLA polymer, dye aggregation (i.e., dye/lactide phase separation) is expected in the former substrate, whereas individual molecule emission is likely in PLA. In this report, we explore the capability of BF_2dbmOMe as an environmentally sensitive dye to monitor lactide polymerization, where a crystalline-to-amorphous transition occurs. For easy comparison with previous dye−polymer conjugate systems (34, 35), the bulk polymerization of DL-lactide was initiated by ethylene glycol and catalyzed by $Sn(oct)_2$ at 130 °C.

EXPERIMENTAL SECTION

Materials. 3,6-Dimethyl-1,4-dioxane-2,5-dione (DL-lactide; Purac Biomaterials, 99.8%) was stored in a drybox under a nitrogen atmosphere and used without further purification. Catalyst tin(II) 2-ethylhexanoate [$Sn(oct)_2$; Spectrum] and initiator ethylene glycol (Sigma-Aldrich, 99.8%) were used as received. Polymer probe BF_2dbmOMe was synthesized as previously reported (41).

Methods. Molecular weights were determined by gel permeation chromatography (GPC) with refractive index (RI) detection (THF; 25 °C, 1.0 mL/min) against polystyrene standards using an autosampler. (PLA molecular weights were multiplied by a 0.58 correction factor (42).) A Polymer Labs 5-μm mixed-C guard column and two GPC columns along with Agilent Technologies instrumentation (series 1100 high-performance liquid chromatograph) were used in GPC analysis. Monomer conversion was calculated from integration of the GPC traces from RI detection corresponding to the polymer and monomer in the aliquots using the following equation: conversion % $= I_{polymer}/(I_{polymer} + 0.89I_{monomer}) \times 100\%$. A correction factor of 0.89 was applied to integration of the monomer peak, to account for the RI differences between lactide monomer and polymer (43). Steady-state fluorescence emission spectra were recorded on a Horiba Fluorolog-3 model FL3-22 spectrofluorometer (double-grating excitation and emission monochromators). Time-correlated single-photon-counting (TCSPC) fluorescence lifetime measurements were performed with a NanoLED-370 (369 nm) excitation source and a DataStation Hub as the SPC controller. All solid-state measurements were performed with front-face detection. Sample X-ray diffraction (XRD; Smart-Lab, Rigaku Inc., Tokyo, Japan) used the Cu Kα radiation wavelength (0.154 nm). The scan was $\theta-2\theta$, ranging from 4 to 40° with a step size of 0.01°.

Lactide Polymerization. Ethylene glycol (1.42 mg, 23.0 μmol), lactide (2.00 g, 13.9 mmol), and $Sn(oct)_2$ (0.37 mg, 0.91 μmol) in hexanes were combined in a sealed Kontes flask under nitrogen in the presence of various amounts of BF_2dbmOMe (6, 15, and 30 mg). The entire bulb of the flask was submerged in a 130 °C oil bath (to prevent the monomer from solidifying on the upper walls of the flask). Aliquots were drawn up into a capillary at the specified times, and then the flask was resealed under nitrogen.

RESULTS AND DISCUSSION

Photophysical Properties of BF_2dbmOMe. BF_2dbmOMe forms yellow crystals that emit greenish-yellow light under UV excitation. The crystals have an emission maximum of 546 nm (Figure 1) and a long-lived fluorescence lifetime of 41 ns. BF_2dbmOMe shows moderate solubility in polyesters such as PLA and PCL. When BF_2dbmOMe (0.1% w/w) is dissolved in PLA, a dramatic hypsochromic shift (λ_{max}

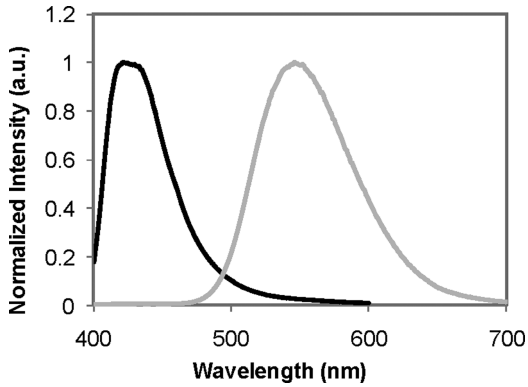


FIGURE 1. Steady-state emission spectra of BF_2dbmOMe in PLA (black) and in the crystalline solid state (gray) (λ_{ex} = 369 nm).

= 421 nm) is observed, accompanied by a sharp reduction in the lifetime (2.0 ns). The difference in the optical properties between the crystalline and PLA-dissolved BF_2dbmOMe molecules may be attributed to the presence and absence of close intermolecular dye−dye interactions.

ROP of DL-Lactide. Bulk polymerization of DL-lactide was carried out at 130 °C with a molar ratio for the initiator (ethylene glycol), monomer (DL-lactide), and catalyst [Sn(oct)$_2$] fixed at 1:150:$^1/_{50}$. Because the initiator is bifunctional, the catalyst to initiating site loading was in fact 1:100 to allow for relatively slow polymerization and, thus, more manageable sampling. Three parallel reactions were run, keeping the amount of DL-lactide monomer at ~2 g, while the amount of BF_2dbmOMe was varied from 6 mg to 15 and 30 mg. To test whether the boron dye influences the polymerization process, a control experiment was performed. PLA molecular weights and percentage monomer conversion were compared at different time points with and without 30 mg of BF_2dbmOMe. On the basis of GPC analysis, the dye did not appear to alter the polymerization kinetics, which indicates that the boron dye optical probe is inert under the reaction conditions.

Monitoring the Polymerization Kinetics with BF_2dbmOMe. Lactide polymerization with 6 mg dye loading was examined. At 130 °C, the dye formed a clear solution in the lactide melt, exhibiting strong blue emission similar to that observed in CH_2Cl_2. One aliquot of the solution was withdrawn into a nonfluorescent capillary tube prior to the addition of the tin catalyst. Upon cooling, the homogenous melt quickly solidified in the thin capillary, forming a yellow polycrystalline mixture. Under UV light, the mixture showed intense yellow emission resembling that of the BF_2dbmOMe crystals. After the catalyst was added to the melt, at designated time points, aliquots of the hot, liquid reaction mixtures were drawn into capillary tubes and the samples solidified upon cooling. As a function of the polymerization time, the solid samples in the capillary tubes exhibited an apparent phase change from polycrystalline to amorphous from XRD patterns (Figure 2), but the XRD patterns for these polymerization mixtures are not a mere combination of lactide and BF_2dbmOMe crystal peaks but are rather complex and lack an obvious trend. Additionally, under UV light, the fluorescence emission transitioned from

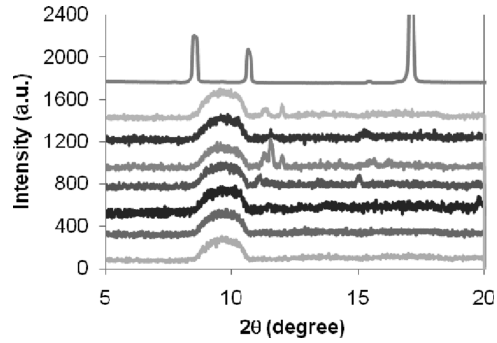


FIGURE 2. XRD patterns of BF_2dbmOMe crystals, lactide solid, reaction mixtures at 5, 10, 30, 60, 300 min, and the capillary tube (top to bottom). (Note: All samples were measured in the capillary tube except for the BF_2dbmOMe crystals, given the high melting temperature of the dye.)

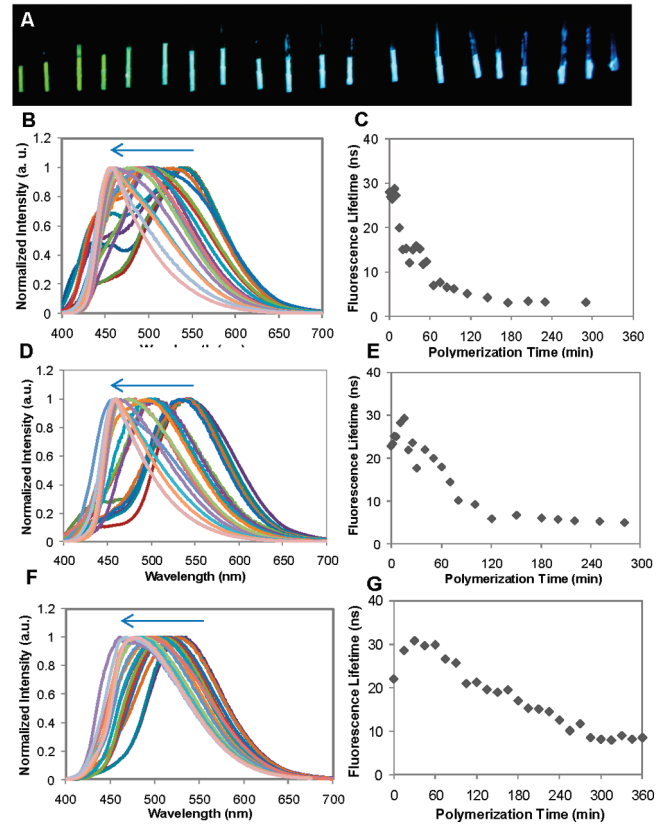


FIGURE 3. Photograph (A) showing solidified polymerization mixtures (6 mg dye loading) in capillary tubes under UV light (λ_{ex} = 365 nm). From left to right (indicated by the arrow), the first sample is a dye/lactide mixture prior to the addition of the tin catalyst. Starting from the second sample, the PLA content starts to increase. Steady-state fluorescence spectra of the solidified polymerization mixtures taken at different polymerization times with 6 mg (B), 15 mg (D), and 30 mg (F) BF_2dbmOMe contents and pre-exponential weighted fluorescence lifetimes vs polymerization time with 6 mg (C), 15 mg (E), and 30 mg (G) BF_2dbmOMe contents.

yellow to blue (Figure 3A) over the course of polymerization. In addition, a strong green "afterglow", namely, RTP, was also observed for the cooled, solidified aliquots, suggesting that the formation of lactide polymers is important for RTP. Only weak RTP is observed for dye/lactide monomer blends.

For the 6 mg BF_2dbmOMe study, each solid sample aliquot was studied by both steady-state fluorescence spectroscopy and lifetime measurements. Consistent with visual

observation, the emission maximum shifted from 544 nm (dye/monomer blend; $t = 0$) to 451 nm (dye/monomer/polymer blend; $t = \sim 180$ min) (Figure 3B) over the course of the reaction. Compared to BF_2dbmOMe crystal fluorescence (FWHM = 81 nm, $\lambda_{max} = 546$ nm), the BF_2dbmOMe/lactide solid blend emission is perceivably broadened (FWHM = 107 nm) and the peak maximum is slightly blue shifted ($\lambda_{max} = 544$ nm). This may be due to many different types of molecular interactions in both ground and excited states. Another feature, namely, a shoulder around ~430 nm typical of optically dilute BF_2dbmOMe emission in organic solvents, is apparent in the $t = 0$, 5, 10, and 15 min samples/blends. The bimodal distribution of the fluorescence spectrum at the onset of the reaction indicates that the boron dye is perhaps dispersed unevenly in the lactide, where most BF_2dbmOMe molecules exist as phase-separated dye clusters (yellow peak), while a small amount may be isolated dye molecules (blue shoulder) dispersed in a lactide monomer. After 20 min, the 430 nm shoulder in the spectrum begins to increase and merge with the major peak at 544 nm, resulting in a compounded spectrum ($\lambda_{em} = 494$ nm). Beyond that time point, single peaks are observed in the spectra, and as polymerization proceeds, the peak becomes narrower and more hypsochromic. Fluorescence lifetime measurements were also performed for all of the sample aliquots at their emission intensity maxima. The preexponential weighted lifetimes first follow a sharper decrease (~30−4 ns) as a function of the polymerization time and then plateau (~4 ns) by $t = 120$ min (~30% monomer conversion) (Figure 3C). The results suggest that, beyond a certain monomer conversion, probe molecules reside in more homogeneous microenvironments, and it is possible that most dye clusters have dissolved as individual fluorophores in the PLA matrix.

For all three polymerizations (BF_2dbmOMe = 6, 15, and 30 mg), the aliquot solids showed yellow emission initially and shifted to blue emission at the end of the polymerization. However, at a given polymerization time, the fluorescence emission of the sample with higher dye content is more red shifted than the lower dye content counterpart, as shown in parts D and F of Figure 3, and the lifetime is longer too (Figure 3E,G). For example, after 15 min, the emission maxima for the polymerization mixtures containing 6, 15, and 30 mg BF_2dbmOMe are 457, 503, and 527 nm, respectively. From the GPC data, the monomer percent conversions of the three samples are all ~5% ($M_n \sim 1.3$ kDa), once again indicating that different dye concentrations do not appear to influence the polymerization kinetics. The observed optical property difference, namely, that higher dye loading causes a red shift in the emission and a longer fluorescence lifetime, may be due to stronger fluorophore−fluorophore interactions in the PLA matrix as previously described (34).

Finally, we examined the fluorescence emission maxima as a function of the monomer percent conversion for the three probe loadings, as shown in Figure 4. For all three sets, the emission maxima show blue shifts as more monomer

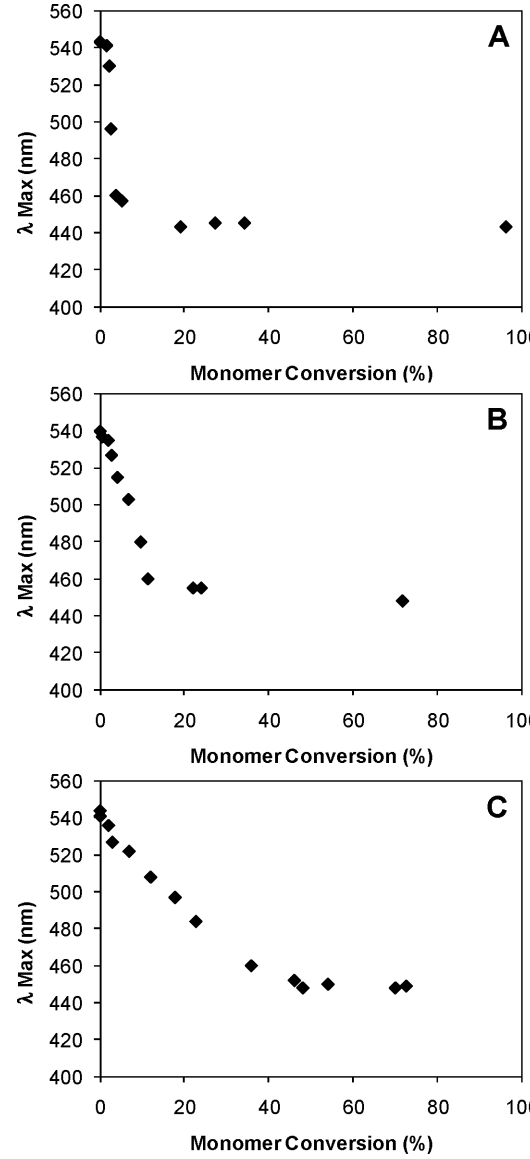


FIGURE 4. Fluorescence emission maxima of the solidified polymerization mixtures versus monomer percent conversions with 6 mg (A), 15 mg (B), and 30 mg (C) BF_2dbmOMe probe loadings.

is polymerized. For polymerization with the lowest dye content, the most rapid blue shift was observed, similar to the lifetime versus polymerization time plot. The detection ranges (via emission colors) at 6, 15, and 30 mg dye loadings are roughly up to 10%, 20%, and 45% monomer conversion, respectively, in roughly linear correspondence with the probe concentrations. A control experiment probing different weight percentages of lactide in PLA (0−100%, in 10% increments) with the dye confirmed that nearly full range optical sensing is possible with higher dye loading (~60 mg). After ~460 nm, the emission maxima drop more gradually to 445−450 nm with increasing monomer conversion (e.g., Figure 4C), similar to previous observations where a more gradual blue shift is noted with increasing polymer molecular weight (i.e., polymer/dye loading) (34). While still informative about monomer conversion, this effect is less dramatic than the contrast between the solid and dissolved probe emission.

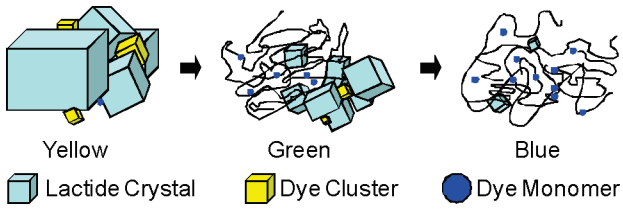


FIGURE 5. Model for the fluorescence color-changing mechanism for the BF_2dbmOMe lactide ROP probe.

DISCUSSION

On the basis of the results, we propose a model to explain the color-changing process, as illustrated in Figure 5. Prior to the addition of the tin catalyst, after cooling, lactide and BF_2dbmOMe phase separate and the dye molecules exist as clusters in the intercrystalline spaces of lactide. This may be due to the poor solubility of BF_2dbmOMe in solid lactide. Although the majority of the dye species form aggregates and emit yellow fluorescence, the blue emission shoulder may arise from a small portion of dye trapped inside the lactide crystals or at the interfaces of the lactide and dye. Thus, at this stage, fluorescence from BF_2dbmOMe is mainly dominated by its solid-state aggregation. This is coincident with the steady-state fluorescence emission spectra of the dye/lactide blends (Figure 3). Regardless of the dye content in the lactide monomer, the spectra are bimodal, with the main peaks at ~540 nm plus shoulders at ~430 nm. In addition, relatively larger high-energy shoulders are noted for lower dye concentrations, suggesting a larger individual-to-aggregate dye ratio than for higher dye loadings where the aggregate emission dominates. The lifetimes monitored at 420 nm are roughly 2 ns, which is close to the lifetime of isolated fluorophores in solution.

Once the ROP starts, PLA starts to form and serves as a better solubilizing medium. Polymers are highly porous materials, and small molecules can easily fit in the interchain spaces. At lower polymer content, PLA might be saturated with BF_2dbmOMe dyes and the emission color may be significantly red-shifted because of stronger fluorophore–fluorophore interactions (34). The green fluorescence plus the yellow emission from the dye clusters therefore produces a bimodal greenish-yellow fluorescence. As the polymerization progresses, dye molecules are increasingly dispersed in the PLA matrix and emit blue light as individual fluorophores. It is also noted that, as a function of the monomer percent conversion (Figure 4), the emission maxima values first drop fast almost linearly and then slowly level off, especially for the most concentrated sample (Figure 4C). This observation also suggests that in the beginning the linear drop could be due to progression of the binary system, i.e., dye probes migrate from aggregates to the PLA solvent. Once the dye molecules are largely solublized in the PLA matrix, additional polymer formed serves as a solid-state solvent to dilute the dye concentration further. The emission spectra gradually blue shift, possibly because of diminished "fluorophore–fluorophore interactions" as previously proposed (34).

On the basis of this hypothesis, the fluorescence emission of the system is determined by the lactide crystal/polymer

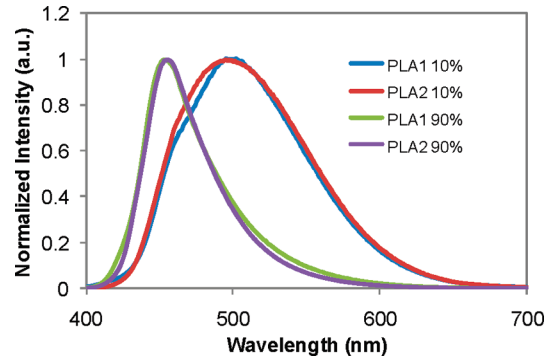


FIGURE 6. Fluorescence emission spectra of polymer/lactide mixtures.

(i.e., bad solvent/good solvent) ratio. If this assumption is true, then as long as the polymer/monomer ratio (w/w) is the same for a given dye loading, the polymer molecular weights should not significantly affect the dye fluorescence. To test this idea, a control experiment was performed. Polylactides of two different molecular weights (PLA1, 5.1 kDa; PLA2, 29.2 kDa) were mixed with DL-lactide at two different ratios in the presence of 0.3% BF_2dbmOMe. The mixtures were heated to 130 °C to form a homogenous melt, and after 5 min, the samples were drawn into a capillary tube. Figure 6 shows that when the polymer content is ~10% for both PLA1 and PLA2, the emission spectra are almost superimposable (λ_{max} ~ 500 nm). Accordingly, their fluorescence lifetimes have close values as well (16.3 and 13.7 ns). The same is true for PLA content = 90%, where similar emission spectra (λ_{max} ~ 450 nm) and lifetimes (3.8 and 3.6 ns) were also observed. Although BF_2dbmOMe fluorescent emission may not be sensitive to PLA molecular weights but rather to the PLA/lactide ratio, nevertheless, this does not preclude its practical use for estimating the lactide percent conversion and thus the calculated molecular weight in controlled polymerizations.

CONCLUSION

In summary, we have described a simple method employing a fluorescent difluoroboron dibenzoylmethane complex, BF_2dbmOMe, as an emission color probe for solvent-free lactide ROP. BF_2dbmOMe is highly fluorescent both as solid aggregates and in polylactide (PLA) substrates with distinctly different emission colors and lifetimes. When BF_2dbmOMe is embedded in crystalline DL-lactide, the dye tends to form clusters that are evident upon visual inspection, but it can dissolve well in PLA. Thus, the inert boron dye can be used as a fluorescent probe to monitor the polymerization of lactide. When small amounts of BF_2dbmOMe are added to the polymerization, sample aliquots exhibited a yellow-to-blue color transition as a function of time, accompanied by a decreasing trend in fluorescence lifetimes. This is in good agreement with the hypothesis that the boron dye may be first emitting as phase-separated dye clusters among the crevices or intercrystalline pores of the lactide and then started to migrate or dissolve in the polymer substrate. To the best of our knowledge, this is the first time that a fluorescent probe has been utilized for both its aggregate and individual molecule emission to monitor

lactide polymerization. Given the importance of lactide polymerization and the simplicity of the method, BF_2dbmOMe and its derivatives could find useful application.

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