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Temperature-Dependent Photophysical Properties of a Liquid-Crystalline Random Copolyester

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We have investigated the temperature-dependent time-resolved fluorescence of Vectra A910, a commercially produced main-chain liquid-crystalline copolyester composed of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA). The experimental temperature range was from -180 to +400 °C, in which all four previously reported phase transitions were observed. At all observed temperatures, the time-resolved fluorescence was found to fit first-order stretched exponential decays. These decays are indicative of inherent disorder based on the random intrachain sequencing of the HBA and HNA subunits and the distribution of torsional angles between adjacent HNA chromophores causing variations of the π -orbital conjugation lengths. The kinetics of the fluorescence emission is rotationally coupled to the HNA chromophores, which can be associated with the observation of two separate temperature realms. The first realm, in which the HNA subunits are rotationally frozen, is characterized by a vibrationally coupled emission only. This realm is distinguished by static disorder within the stretched exponential envelope. In the second-higher temperature realm, the HNA torsional rotations feature both vibrationally and rotationally coupled excited-state relaxation. The rotational coupling manifests as dynamic disorder in the stretched exponential decays. The dynamic disorder is indicative by a broadening of the rotational distribution with increased temperature. The second temperaturedependent realm can be further characterized by a classical Arrhenius behavior leading to an activation energy of 1.357 kcal/mol (474.9 cm⁻¹ or 0.05885 eV).

Introduction

In this paper, we continue our earlier investigation¹ into the photophysical characterization of the liquid-crystalline random copolyester, commercially known as Vectra A910. Our previous study sought to understand the optical and photophysical properties of a main-chain thermotropic liquid-crystalline random copolyester composed of 73% 4-hydroxybenzoic acid (HBA) and 27% 6-hydroxy-2-naphthoic acid (HNA), as shown in Scheme 1, commonly known in the literature as copoly(HBA/HNA).

In our previous work, we employed steady-state UV-vis absorption, FT-IR, FT-Raman, and second-harmonic generation, as well as steady-state and time-resolved photoluminescence, to characterize the optical and photophysical properties of copoly(HBA/HNA). These experimental techniques gave macroscopic evidence for long highly aligned polymeric chains, which possess strong absorption abilities in the UV range, with a broad extended tail leading far into the near-infrared.

Although the two monomeric subunits, HBA and HNA, are randomly sequenced within the primary structure of a single main-chain, the nature of the chemical bonding produces a tandem directionality with the net permanent dipole uniaxially oriented along the direction of a single polyester chain. This tandem uniaxial arrangement of the permanent dipole imposes a loss of the center of symmetry, and thus imparts a strong and





resonance-stabilized second-harmonic response, as originally proposed by Asada et al.^{2,3} and Watanabe et al.⁴

The steady-state photoluminescent excitation maximum was found to be 376 nm (3.30 eV) with a strong and highly efficient fluorescent emission maximum at 428 nm (2.90 eV) and weak phosphorescent emission maximum at 525 nm (2.36 eV).⁵ The time-resolved fluorescence emissions fit well to a first-order stretched exponential decay, which revealed an emission lifetime of 2.57 \pm 0.02 ns with a stretching coefficient of 0.78 \pm 0.002.¹

The goal of this paper is to continue the photophysical characterization of copoly(HBA/HNA) by studying the time-resolved fluorescence in the temperature range from -180 to +400 °C. We have confirmed that the time-resolved fluorescence kinetics of copoly(HBA/HNA) are well described by first-order stretched exponential decays within the stated temperature range. The physical nature of these decays indicate significant disorder innate to this copolyester. These temperature-dependent studies will take into account a photophysical mechanism of the disorder inherent to the fluorescence emission.

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Background

It is appropriate to provide an overview of the concepts and mathematics of the first-order stretched exponential decay. This will invariably lead to the physical interpretation of the disorder inherent in systems characterized by this decay function. The first-order stretched exponential function is expressed as

$$I(t) = I(0) \exp(-(t/\tau_{ww})^{\alpha})$$
(1)

where I(t) is the intensity at time t, I(0) is the intensity at the initial time 0, τ_{ww} is the Williams–Watts lifetime, and α is the stretching coefficient, ranging from zero to one, with the value of one yielding the classical first-order exponential decay. If I(0) is normalized to unity, then eq 1 may be rewritten simply as

$$I(t) = \exp(-(t/\tau_{\rm ww})^{\alpha})$$
(2)

If I(t) is considered as arising from a superposition of exponential decays, then eq 2 can be rewritten as

$$\exp(-(t/\tau_{\rm ww})^{\alpha}) = \int_0^\infty \exp(-t/\tau) \cdot \rho_{\rm ww}(\tau) \, \mathrm{d}\tau \qquad (3)$$

where $\rho_{ww}(\tau)$ defines the distribution function of the Williams– Watts decay. Lindsey et al.⁶ and Montroll et al.⁷ rewrote the above expression as

$$\exp(-s^{\alpha}) = \int_0^\infty \exp(-sx) \cdot \lambda(x, \alpha) \, \mathrm{d}x \tag{4}$$

where $\lambda(x,\alpha)$ is the inverse Laplace transform of $\exp(-s^{\alpha})$. Using the substitutions

$$x = \tau_{ww}/\tau$$

$$s = t/\tau_{ww}$$

$$\lambda(x,\alpha) = \frac{\tau_{ww}}{x^2} \cdot \rho_{ww} \left(\frac{\tau_{ww}}{x}\right)$$
(5)

one can find through contour-integration

$$\lambda(x,\alpha) = \frac{1}{\pi} \int_0^\infty \exp(-xu) \cdot \exp[-u^\alpha \cos(\pi\alpha)] \cdot \sin[u^\alpha \sin(\pi\alpha)] \, du$$
 (6)

and thus

$$\rho_{\rm ww}(\tau) = \frac{\tau_{\rm ww}}{\tau^2} \cdot \lambda \left(\frac{\tau_{\rm ww}}{\tau}, \alpha \right) \tag{7}$$

which can be numerically evaluated using computer software such as Mathematica by Wolfram Research. The probability $\rho_{ww}(\tau)$ is for the relaxation occurring at a particular lifetime τ . Therefore, if one assumes a Williams–Watts lifetime τ_{ww} of unity, then a plot of eq 7 will reveal the distribution curve for lifetimes τ at a particular stretching coefficient. The probability density $\tau \rho(\tau)$ is plotted as a function of τ/τ_{ww} , as seen in Figure 1. A stretching coefficient of unity, and thus a classical firstorder exponential decay, would appear in Figure 1 as a delta function centered at one. In this case, there would not be a distribution of lifetimes. Therefore, in general, the above treatment reveals that for a decreasing stretching coefficient less than one, the distribution of relaxation lifetimes increases. For a stretching coefficient of 0.78, Figure 2 is a linear–linear plot



Figure 1. Probability density for the indicated stretching coefficients assuming a William–Watts lifetime τ_{ww} of unity for the first-order stretched exponential decay.



Figure 2. Probability density for copoly(HBA/HNA), assuming a William–Watts lifetime τ_{ww} of unity.

of the probability density for copoly(HBA/HNA) at ambient conditions. For a Williams—Watts lifetime τ of 1 ns, the lifetime distribution of copoly(HBA/HNA) is a skewed Gaussian distribution with a most probable lifetime around 1.5 ns and full width at half-maximum of 1.4 ns.

Experimental Section

The extruded polymer films of copoly(HBA/HNA) with a molar composition of 73/27 were supplied by Celanese Limited, Charlotte, NC. The films of 75 μ m thickness used in these experiments are the Celanese high purity research-grade Vectra A910. X-ray and mechanical measurements of this material have been previously reported in the literature.^{8–15}

The time-resolved fluorescence measurements were performed using a Hamamatsu Streak Camera Model C5680. Spectra were obtained from 420 nm (2.95 eV) to 700 nm (1.77 eV). A 420 nm (2.95 eV) long wavelength pass filter was used to block the 400 nm (3.10 eV) incident laser light. The experimental time resolution was about 80 ps, limited by jitter in the triggering electronics. This time resolution was sufficient to precisely measure the emission kinetics of the copoly(HBA/



Figure 3. Temperature-dependent fluorescence emission maxima of a 75 μ m copoly(HBA/HNA) extruded thin film at ambient pressure. T(A) and T(B) correspond to the local HBA torsions, T(C) to the local HNA torsions, T(D) to the copolyester's glass transition, and T(E) corresponds to the crystalline melt. See the text for further details.

HNA) fluorescence reported herein. Typically, less than 1 mW of 400 nm (3.10 eV) light was used to excite the copolyester thin-film samples.

The temperature apparatus within the range of -180 to +160 °C was a nitrogen cooled cryostat. A feedback-controlled heating element was placed directly behind the copoly(HBA/HNA) sample in which the temperature was measured using a standard Omega Type T thermocouple. The temperature apparatus within the range of +50 to +400 °C was a high-temperature hotplate manufactured by Thermolyne, Model HP72625. An oxygenfree copper sample holder was fabricated to mount the copoly(HBA/HNA) sample and thermally couple it to the hotplate. The temperature was also controlled using temperature feedback circuitry and measured using an Omega Type K thermocouple. Overlapping temperature ranges, from +50 to +160 °C, were used to confirm the results and consistency between the cryostat and hotplate methods, as seen in Figure 3.

Results and Discussion

Wavelength-Dependent Fluorescence. Time-resolved spectra were obtained between -180 and 340 °C inclusively, in 10 °C increments, yielding a minimum of 53 temperature-dependent spectra. The Hamamatsu Streak Camera permits the simultaneous acquisition of the time, wavelength, and respective intensity data that may be processed as a 3D contour map. Therefore, each time-resolved spectrum has the potential to contain a great deal of information. To understand this large amount of data, each wavelength-dependent spectrum was acquired and the fluorescence emission maximum was plotted against the sample temperature, as shown in Figure 3.

Previous literature, $^{15-23}$ using various experimental techniques, report four phase transitions and their respective temperatures, for 73:27 copoly(HBA/HNA), as summarized in Table 1. The shifts and drifts of emission maxima in Figure 3 correspond to these reported phase transitions. The experimental technique, developed herein, to generate the data presented in Figure 3 was not meant to establish the phase transitions. However, correlation of these data with the latter published phase transitions could provide insight into the molecular-level photophysics involved with copoly(HBA/HNA). Further developmentations are supported with copoly(HBA/HNA).

 TABLE 1: Phase Transitions for Copoly(HBA/HNA) under

 Atmospheric Pressure

phase transition	temperature (°C)	symbol
crystalline melt	+280	$T_{ m m}$
glass or amorphous melt	+100	$T_{\rm g}$ or α
local HNA rotations	+25	β
local HBA rotations	-60	γ

opment of this technique to increase the temperature resolution and signal-to-noise ratio may allow for such phase transition determinations.

Phase transitions at -60 °C, indicated by T(A) and T(B), correspond to the γ phase transition or the local HBA torsions.^{17,19,20} Dielectric relaxation¹⁹ studies of the γ phase transition suggest two motions that may be resolved in Figure 3 as two discrete sharp shifts, T(A) and T(B). Alhaj-Mohammed et al.¹⁹ suggested a lower energy librational motion due to the steric hindrance about the ester—aromatic bonds. This librational motion could correspond to the T(A) shift in Figure 3. A higher thermal energy would be required to overcome the steric hindrance and allow for a full local HBA rotation, as suggested by the T(B) shift.

Phase transitions at 25 °C, indicated by the T(C) drift, correspond to the β transition or the local HNA torsions.^{15–17,19,20} Yoon et al.²⁰ via dielectric relaxation, and Green et al.¹⁶ by thermal expansion, found that the β transition has a glass transition component that is accompanied by reduced conformational constraints. The weak presence of this glass transition component at room temperature corresponds to the gradual emission shift at T(C).

The fluorescence emission maxima reach a minimum at 100 °C, as indicated by the T(D) drift, which corresponds to the T_g phase transition or the copolyester's glass transition.^{15–17,19} Thermal expansion¹⁶ plots revealed that the axial expansion was small but negative, corresponding to contraction in the direction of nematic director. The lateral expansion was large and positive, denoting rapid expansion perpendicular to the nematic director. Therefore, the copolyester is contracting axially and expanding laterally, in which case the effect is amplified once the copoly-(HBA/HNA) reaches 100 °C. These results indicate that the thermal expansion is based on intrachain molecular segments rotating in concert, otherwise known as a segmental crankshaft motion.²⁴

Finally, the huge emission shift at 280 °C, as indicated by T(E), corresponds to the T_m phase transition or the crystalline melt.^{15,19,20,23} This melt is characterized by a macroscopic shrinkage of the polymer along the nematic director, with disorientation and full translational motion of the molecular chains. The fluorescence emission at these high temperatures clearly revealed energy loss due to thermal processes being the preferred mechanisms over luminescent pathways. This was observed by a greatly reduced emission intensity and huge redshifting of the emission maxima. This red-shift may be due to phosphorescence emission being the preferred photoluminescent pathway, as seen in ambient steady-state studies.⁵

The temperature-dependent emission maxima, Figure 3, provides insight into the molecular-level photophysics involved in copoly(HBA/HNA). In addition to the apparent red-shift caused by the HBA rotations, our data indicate that the full width at half-maximum (fwhm) of the emission spectra for the T(A) and T(B) regions are on the average 140 nm. The totally frozen region, -180 to -80 °C, and the region between -10 and +240 °C, have on the average a fwhm of 80 nm. Therefore, the HBA rotations broaden the emission profile as compared to the other temperature regions. The red-shift and the broadening as induced



Figure 4. Absorption spectra of HBA in 1 mM ethanol (**A**), HNA in 1 mM ethanol (**B**), and 10 μ m copoly(HBA/HNA) film (**C**) at ambient conditions. Reproduced from Lukacs et al.¹



Figure 5. The stretching coefficient α versus temperature for a 75 μ m copoly(HBA/HNA) extruded thin film at ambient pressure.

by the HBA rotations are indicative of spectral diffusion, which is primarily caused by a distribution of local environments around an excited chromophore. The HBA rotations, therefore, enhance the spectral diffusion within copoly(HBA/HNA).

The absorption spectrum of copoly(HBA/HNA), Figure 4 C, in which the broad ultraviolet absorption not only encompasses the absorption profiles of the HBA and HNA monomers, Figure 4, parts A and B, respectively, but its red-shifted edge and its long extended tail provide further evidence to the enhancement of spectral diffusion in the copolyester in general. The long tail extends into the near-infrared region as observed in the FT-Raman of copoly(HBA/HNA).¹

This interpretation of spectral diffusion is supported by similar absorption and fluorescence studies performed by Bässler's group^{25–27} and Kauffmann's group.²⁸ Their studies on π -conjugated copolymers of poly(*p*-phenylene vinylene) (PPV), and like materials, indicate a strong red-shifted emission as compared with the absorption peak, a broad fluorescence emission profile, as well as an inhomogeneously broadened absorption profile as derived from homologous oligomers. These effects have been interpreted as an array of chromophores separated by topological faults leading to inhomogeneously broadened density of state distributions arising from variations in the conjugation length and local environment. Further, time-resolved fluorescence



Figure 6. The Williams–Watts lifetime τ versus temperature for a 75 μ m copoly(HBA/HNA) extruded thin film at ambient pressure.



Figure 7. Arrhenius plot of the Williams–Watts lifetime τ for a 75 μ m copoly(HBA/HNA) extruded thin film at ambient pressure.

studies of PPV revealed the inherent nonexponential behavior indicative of energetic disorder. The latter is the topic of study for copoly(HBA/HNA) in the next section.

Time-Resolved Fluorescence. The 3D contour maps discussed above were further processed to acquire the time-resolved data for each temperature in the range of -180 to 340 °C. The procedure of fitting the first-order stretched exponential decays are outlined in our previous paper.¹ All linearized ln(ln(*I*(0)/*I*(*t*))) versus ln(*t*) plots in these experiments exhibited a correlation coefficient of 0.94 or better. The linear fits were used to directly derive the stretching coefficient α and the Williams–Watts lifetime τ , as shown in Figures 5 and Figure 6, respectively.

Figures 5 and 6 demonstrate a similar behavior in which the stretching coefficient α and lifetime τ , respectively, possess two regions. The first region is characterized by constant temperatures less than approximately 25 °C. The second region displays a linearly decreasing temperature-dependent region, at temperatures greater than 25 °C. These regions can be more easily viewed by plotting the lifetime τ in a classical Arrhenius plot, which is ln(rate) versus 1/T, as seen in Figure 7. The temper-



Figure 8. Arrhenius plot of the temperature-dependent realm for the Williams–Watts lifetime τ for a 75 μ m copoly(HBA/HNA) extruded thin film at ambient pressure.

ature-dependent realm was extracted from this plot and rescaled, as seen in Figure 8.

In many respects, copoly(HBA/HNA) is similar to PPV. Chemically they are main-chain random copolymers composed of π -conjugated aromatic monomeric subunits. They both exhibit similar spectral diffusion, as discussed above, and stretched exponential fluorescence decays. The similar chemical structures and optical responses between copoly(HBA/HNA) and PPV allow for similar molecular level interpretation.

Fluorescence emission occurs from the singlet excited-state S_1 to the singlet ground-state S_0 of the chromophore with the elementary excitation being a Coulomb-bound electron—hole pair.^{26,29} The electron—hole migration is dependent on the variations of length and environment of the π -orbital conjugated segments. The intrachain conjugation length depends on the degree of π -orbital overlap between adjacent subunits. The degree of π -orbital overlap throughout the sample will depend on the distribution of rotational-based planarity between adjacent monomeric subunits. The rate of excitation energy transport due to the distribution of rotational conformations are experimentally expressed in the fluorescence emission via a superposition of exponential decays, the first-order stretched exponential decay, as modeled by Kauffmann et al.^{30–33}

Figure 7 clearly delineates the presence of two realms, a temperature-independent and temperature-dependent realm. The transition between the two temperature realms lies in the range of the local HNA torsional motions, which corresponds to the room-temperature β phase transition. The temperature-independent realm includes the γ phase transition of the local HBA torsional motions. Therefore the HBA rotations do not affect the stretching coefficient or the lifetime of the fluorescence emission.

The low temperature-independent realm is based on the vibrationally coupled relaxation of the rotationally frozen HNA chromophores. The stretching coefficient is constant and less than unity, in which the disorder is due to the distribution of frozen rotationally averaged conformations of the HNA subunits. The rotational distribution, as well as the intrachain random sequencing, leads to a distribution of conjugation lengths. Therefore, the distribution of rotationally dependent π -orbital overlaps, will exhibit a fluorescence emission with a constant

disorder and lifetime through a change in temperature. It can be envisioned that the excitation energy migrates through various local topological environments owing to the expression as a superposition of decay energies and thus lifetimes.

The high temperature-dependent realm, that above the β phase transition, is dependent on the vibrationally and rotationally coupled relaxation of the HNA chromophores. The stretching coefficient is decreasing with increasing temperature, in which the increasing disorder is due to the increased distribution of rotationally averaged conformations of the HNA subunits. It can be envisioned that the excitation energy migration is further impaired by the broadening of the rotational-coupling, therefore decreasing the lifetime, as seen in Figure 6.

The temperature-dependent region, Figure 8, follows the classical Arrhenius equation in which the rate of the relaxation is inversely proportional to the temperature. The Arrhenius fit of the temperature-dependent realm revealed an activation energy of 1.357 kcal/mol (474.9 cm⁻¹ or 0.05885 eV). This observation may correspond to the dissociation energy of the Coulomb-bound electron-hole pair as observed in PPV by Bässler et al.^{27,34,35} If the above activation energy is indeed the dissociation energy for the Coulomb-bound electron-hole pair in copoly(HBA/HNA), then comparison of this value to that of Bässler's 0.4 eV for PPV leads to a difference by an order of magnitude. This difference can be attributed to the strong permanent dipole moment inherent in copoly(HBA/HNA), whereas a strong permanent dipole is not an inherent characteristic of PPV. The existence of the strong permanent dipole moment would lower the dissociation energy of the electronhole pair as compared to PPV, which is consistent with the above data. Further investigation to confirm the assignment of this Arrhenius activation energy with the dissociation energy of the Coulomb-bound electron-hole pair for copoly(HBA/ HNA) would be via photoconductivity to measure the free charge production.

Summary

The temperature-dependent spectra of copoly(HBA/HNA) correlate well with the previously reported phase transitions. The absorption and fluorescence spectra reveal the presence of spectral diffusion, due to energy migration along the variations of the π -orbital conjugation lengths and environments of the HNA chromophore. The primary contributor of the variations arise from the distributions of the static and/or dynamic rotational conformations between adjacent HNA subunits. Dynamic disorder is induced at a temperature above the HNA torsion, in which the disorder increases and the lifetime of the emission decreases, with increasing temperature. This classical Arrhenius treatment yields an activation energy of 1.357 kcal/mol (474.9 cm⁻¹ or 0.05885 eV).

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