

Triplet energy transport of liquid crystalline poly(dodecene sulphone)s

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Summary

The geometric arrangement of liquid crystalline poly(dodecene sulphone)s containing cholestanyl pentenoic ester chemically bonded in the side-chains was characterized by monitoring the triplet transport via both steady-state emissions and decays of delayed fluorescence and phosphorescence. The increase in the mesogenic cholestanyl pentenoic side-chains shows an increase in the heterogeneity exponent or degree of disorder, h , which is greater than zero, suggesting that the explored system exhibits the non-classical diffusion-limited or fractal-like transport. The value of h is highly sensitive to the ratio of mesogenic to olefinic side-chains.

Introduction

Polymer luminescence and photophysics have been reviewed for the application of studying the morphology or ordering of polymer chains via aromatic chromophoric probes such as naphthalene and carbazole functional groups, which are covalently bonded onto the polymer backbone (1). Polymer chain interpenetration in solution and solid films prepared under freeze-drying was studied through energy transfer technique (2). Specifically, delayed fluorescence (3) and the phosphorescence lifetime (4) of chromophores doped homopolymers at various dopant concentrations and temperatures were also extensively studied. Furthermore, time-resolved luminescence technique was applied to characterize aromatic chromophores doped in crystalline and liquid states (5) as well as phase transitions in polymer liquid crystals (6). The monitoring of both phosphorescence and delayed fluorescence kinetics in naphthalene-doped PMMA system was employed to determine the effective spectral dimension (7), which was later observed to be related to the morphology of polymer blend consisting of poly(vinyl naphthalene) and PMMA (8).

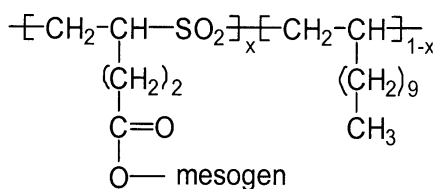
In this study, a series of poly(dodecene sulphone)s containing liquid crystalline cholestanyl pentenoic ester were synthesized. The ratio of liquid crystalline to olefinic side-chains was controlled to obtain a variety of structural disorder, which was monitored by the application of triplet energy transport kinetics via both delayed fluorescence and phosphorescence as described in the previous publication (8).

Experimental

Sample preparation

A series of polysulfone terpolymers containing mesogenic cholestanyl pentenoic ester were synthesized using the method reported before (9). The polymers we studied have the general formula:

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where x is the mole fraction of residues from mesogenic olefins in the chain, and the mesogen is from cholestanol, which is also the chromophore we investigated.

The molecular weights of the terpolymers were measured by using a GPC system (Waters 510 HPLC pump and Waters 410 differential refractometer) with a PL 5 μm C-mixed column (mol wt: $1 \times 10^4 - 1 \times 10^6$) and a PL 5 μm 103 A column (mol wt: $5 \times 10^2 \sim 1 \times 10^4$) respectively. The GPC system had been calibrated with narrow molecular weight standards of polystyrene. The flow rate of carrier solvent, tetrahydrofuran, was 1.0 ml/min and pump pressure was 700 psi. The compositions of the polymers were measured by elemental analysis and confirmed by NMR. Table 1 summarizes the results of the polymer characterization.

Thin films of about 0.1 mm thickness of CSD6 to CSD10 and pure poly(dodecane sulfone) (i.e. without mesogen) were prepared by solvent casting technique respectively. Each sample (~50 mg) was first dissolved in spectral-grade methylene chloride (0.5 ml) and then the solution was casted onto a quartz plate at 298 K. The sample films were subsequently dried in a vacuum oven at about 333 K for at least 2 days for the removal of residual solvent. The prepared sample films appeared to be uniformly translucent and were kept in a desiccator before measurements. Liquid crystalline cholesteric phases were observed in these films when examined under a hot stage polarizing microscope.

Absorption and emission spectra measurement

The room temperature fluorescence spectra of the samples were obtained by using an Oriel 7720 spectrometer and the absorption spectra were acquired by using a Perkin-Elmer Lambda 18 spectrometer. The quartz substrate shows no appreciable absorption due to hydroxyl ions. The sample films were mounted in an immersion type cryostat filled with liquid nitrogen for 77K measurements. The emission spectra of the samples at 77K were obtained by a SPEX Fluorolog spectrometer in connection with a SPEX 1681 monochromator. The excitation source was chosen at 266 nm which is the same wavelength of the fourth harmonic of the Nd⁺-YAG laser.

Delayed fluorescence and phosphorescence decays measurement

Figure 1 shows the schematic diagram of delayed fluorescence and phosphorescence decays detection system. The excitation source was the fourth harmonic of a pulsed Nd⁺-YAG laser (Spectra-Physics GCR-16S) with 10 ns pulse duration. The dominant intensities

Table 1: Compositions and molecular weights of the polysulfone terpolymers

Sample	C%	H%	Mole % of mesogen in polymer	Number-average mol wt
CSD6	65.82	10.46	16.25	4400
CSD7	68.43	10.51	30.92	14000
CSD8	69.64	10.50	41.20	17500
CSD9	70.51	10.56	45.48	39200
CSD10	71.48	10.53	100.0	41000

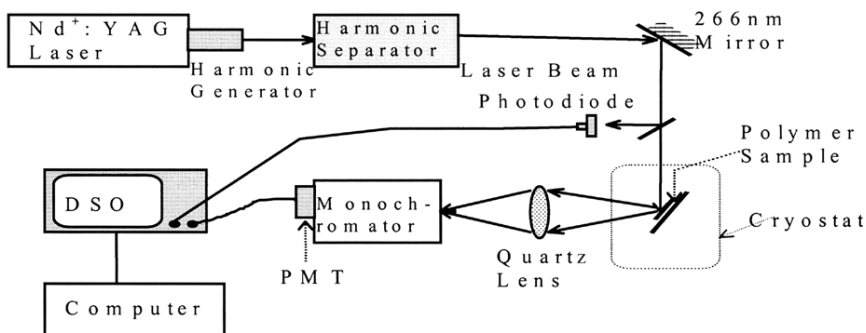


Figure 1: Schematics for detecting delayed fluorescence and phosphorescence decays

of delayed fluorescence and phosphorescence were at 384 nm and 500 nm respectively. The decay time profiles of the samples at these two peaks were detected with a PMT and recorded with a digitized storage oscilloscope (HP5451B, 300 MHz bandwidth). It takes the average of 50 to 80 pulses in each measurement. Each captured decay time profile was digitized to, 1024 data points and transferred to a microcomputer for further analysis.

Curve fitting

All time-dependent decay intensities of delayed fluorescence and phosphorescence measuring at 77K were fitted with a weighted sum of two exponentials as follows:

$$I(t) = A \exp(-t/\tau_1) + (1-A)\exp(-t/\tau_2) \quad [1]$$

whereas A is a weighting factor, τ_1 and τ_2 are, respectively, the short-lived and long-lived lifetimes of excitons. A MicroCal Origin 3.5 program was used for all curve fittings. χ^2 , residuals, and correlation coefficients were used for the judgement of the value of fitting.

Results and discussion

Figure 2 shows the absorption spectrum of CSD10 monitored in the range of 230 - 600 nm at 298K, indicating the typical absorption characteristics of liquid crystalline poly(dodecene sulphone)s containing cholestanyl pentenoic ester. An absorption band in the range of 400 to 500 nm, which is at a much longer wavelength than the emission band, is observed. This may be due to the formation of dimers. The absorption spectra for pure polysulphone and CSD10 in methylene chloride are shown in Figure 3. The strong absorption peak at 266 nm is adopted for the excitation of this series of samples. Figure 3 also shows their fluorescence spectra, which indicate strong and broad emissions ranging from 300 to 400 nm. Figures 4 and 5 show, respectively, the emission spectra of CSD6-10 at 298K and 77K under steady-state excitation. Emissions ranging from 310 nm to 450 nm are considered to be prompt fluorescence (PF) and delayed fluorescence which may well overlay with each other. PF is the result of radiation decay of singlet excited states to singlet ground state. In contrast, delayed fluorescence is generated via the annihilation of two excited triplets which, in turn, produces an excited singlet emitting the same radiation energy as PF (8). Thus, the only difference between PF and delayed fluorescence is the decay time and generation time. Upon steady-state excitation at 298K, only PF is observed and no delayed fluorescence is measured as confirmed by no decay detection as a function of time.

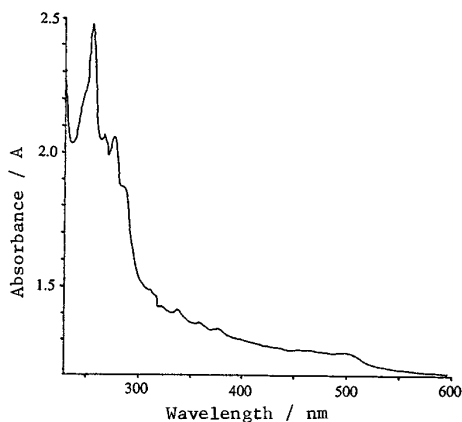


Figure 2: Absorption spectrum of CSD 10 (thin film) at 298K

Moreover, emissions ranging from 450 - 600 nm should be phosphorescence which arises from the inter-system crossing of the excited singlet to triplet and the subsequent radiation decay of triplet to singlet ground state. No phosphorescence is observed at 298K as shown in Figure 4, implying insufficient triplet population and fast thermal deactivation of the triplet state. However, both phosphorescence and delayed fluorescence are observed at 77K under steady-state excitation at 266 nm as shown in Figure 5. It is more obvious to observe the enhancement of phosphorescence and delayed fluorescence at the expense of PF by overlaying the emission spectra of CSD8 obtained at 77K and 298K respectively as shown in Figure 6. As the mesogen concentration in the side chains increases from 16.25% to 100% (CSD6 to CSD10), peak broadening and emission peaks shifting towards short wavelength are observed. In addition, the decrease of 320 nm emission band originating from both pure polysulfone and mesogen side chains as shown in Figure 3 may be due to some kind of irregularities or certain extent of reabsorption. Nevertheless, such irregularities do not interfere with the investigation of monitoring decays and heterogeneity.

At 266 nm excitation under 77K and 298K, no measurable decay can be obtained from 100% pure poly(dodecene sulphone) without the presence of mesogenic cholestanyl ester.

Figure 7 shows the delayed fluorescence and phosphorescence decays acquired at 77K for CSD10. It is observed that delayed fluorescence decays much faster than phosphorescence, implying that there are some trapped triplet excitons, incapable of achieving triplet-triplet fusion, undergoing phosphorescence decays at longer time scale above 5 seconds. A weighted sum of two exponentials model, as described in equation [1], is applied to fit the experimental data. The fitting parameters of all samples for delayed fluorescence and phosphorescence are listed respectively in Tables 2 and 3.

As shown in Tables 2 and 3, both short-lived and long-lived excitons from delayed fluorescence decays show an increase in lifetimes as the concentration of the mesogen increases and vice versa in phosphorescence decays, suggesting that the triplet transport becomes more efficient as the mesogen concentration increases. Table 4 shows the computed heterogeneity exponent via plotting natural logarithm of the ratio of delayed fluorescence to phosphorescence decays versus natural logarithm of decay time as shown

in Figure 8 (8). The slope obtained is the negative heterogeneity exponent (i.e. $-h$). A consistent change of heterogeneity exponent is observed from 0.58 to 0.74 as the mole % of the mesogen varies from 16.25% to 100%. The non-zero h value strongly suggests that the transport is non-classical fractal-like kinetics in contrast to the classical dynamics of the three-dimensional Euclidean homogeneous system such as single crystal (8).

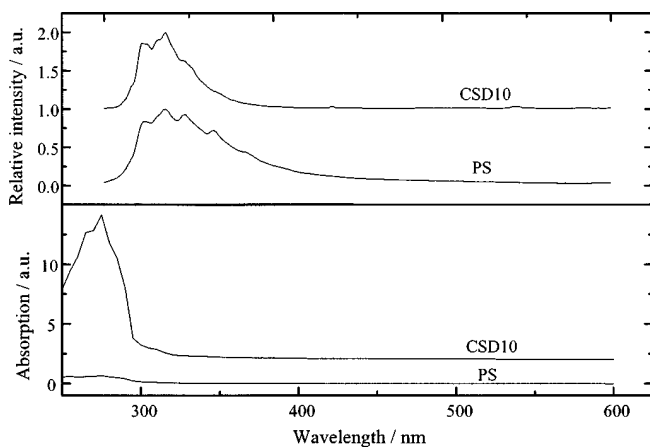


Figure 3: Emission and absorption spectra of pure polysulphone (PS) and CSD10 in methylene chloride (3 g/L) at 298K

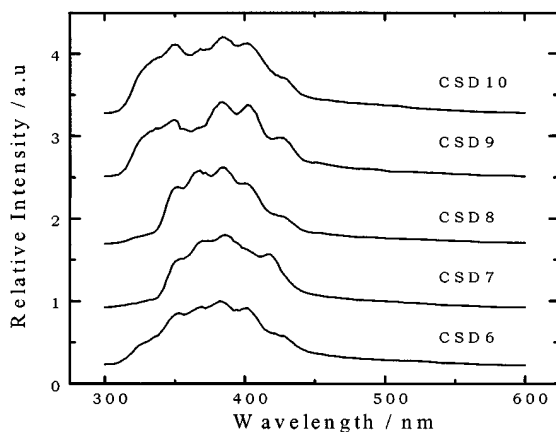


Figure 4: Emission spectra of liquid crystalline poly(dodecene sulphone)s at 298K

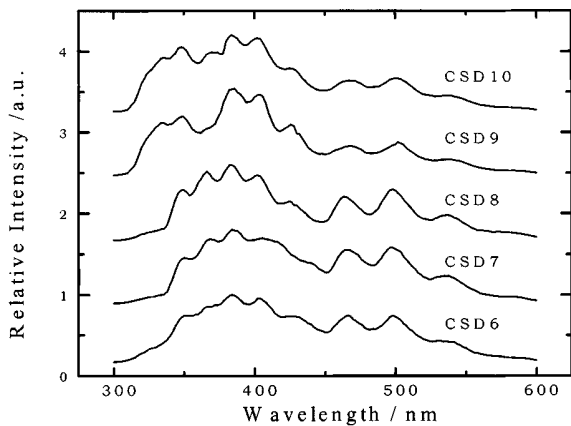


Figure 5: Emission spectra of liquid crystalline poly(dodecene sulphone)s at 77K

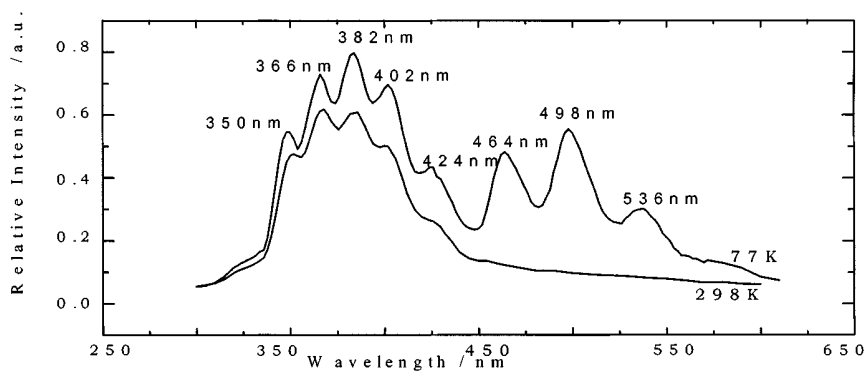


Figure 6: Emission spectra of CSD8 at 77K and 298K

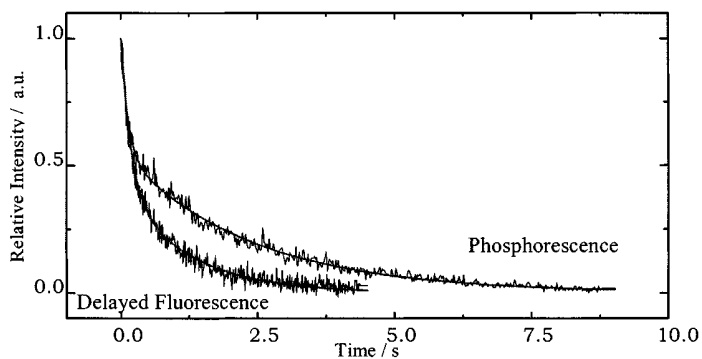


Figure 7: Delayed fluorescence and phosphorescence of CSD10 at 77K

Table 2: Fitting parameters for delayed fluorescence decays

Sample	A	τ_1	τ_2	χ^2	Correlation coefficient
CSD6	0.71	0.06	0.91	0.00070	0.97332
CSD7	0.72	0.09	1.02	0.00046	0.98591
CSD8	0.69	0.10	1.21	0.00083	0.97727
CSD9	0.62	0.11	0.89	0.00057	0.98723
CSD10	0.58	0.18	1.21	0.00047	0.99186

Table 3: Fitting parameters for phosphorescence decays

Sample	A	τ_1	τ_2	χ^2	Correlation coefficient
CSD6	0.37	0.36	2.74	0.00042	0.99477
CSD7	0.39	0.27	2.60	0.00035	0.99510
CSD8	0.42	0.21	2.47	0.00380	0.99373
CSD9	0.44	0.11	2.31	0.00025	0.99522
CSD10	0.57	0.14	2.54	0.00042	0.98945

Table 4: Determination of heterogeneity exponent, h

Sample	Heterogeneity factor, h	Residual	Standard deviation
CSD6	0.58	-0.56233	0.22450
CSD7	0.64	-0.54714	0.27007
CSD8	0.70	-0.47599	0.36602
CSD9	0.73	-0.63840	0.25046
CSD10	0.74	-0.66875	0.17228

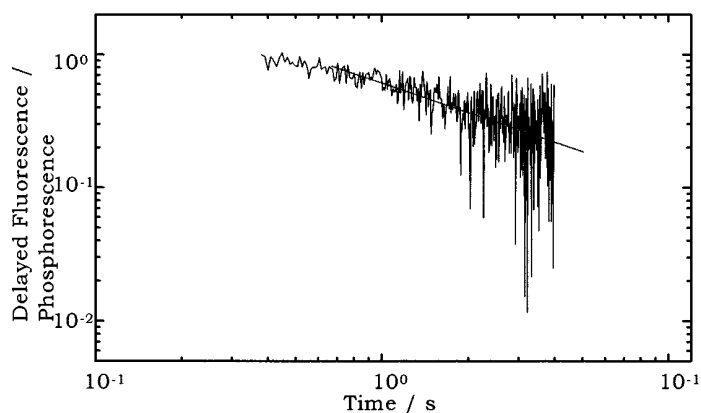


Figure 8: Ratio of delayed fluorescence to phosphorescence decay versus decay time for CSD10 at 77K

Conclusion

The triplet transport of the liquid crystalline sulphones in terms of delayed fluorescence and phosphorescence decays is observed at 77K. From the 298K steady-state emission spectra excited at 266 nm, there is no phosphorescence emissions in the range of 450 to 600 nm. However, strong phosphorescence is observed in the 77K steady-state emission spectra. A weighted sum of two exponentials model is applied to fit the non-exponential delayed fluorescence and phosphorescence decays. In delayed fluorescence decays, both short-lived and long-lived excitons show an increase in lifetimes as the concentration of the mesogen increases and vice versa in phosphorescence decays. It is also observed that a consistent change of heterogeneity from 0.58 to 0.74 as the mole % of the mesogen varies from 16.25% to 100%, which strongly suggests that the observed transport resembles the non-classical diffusion limited or fractal-like transport. Hence, the monitoring of triplet transport via delayed fluorescence and phosphorescence decays to determine the heterogeneity exponent is a useful and sensitive tool in characterizing the degree of disorder of the polymer systems.

Acknowledgement

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