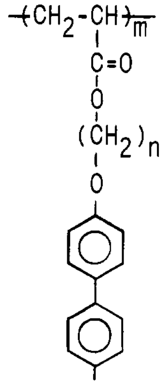
Emission Properties of Polymer Liquid Crystals with Side-Chain Mesogenic Cyanobiphenyls in Solution

Polymer liquid crystals (PLC) have attracted much attention because of scientific interest and because they have numerous technological applications. From a fundamental viewpoint, this interest has been evident in studies of structural dependence on liquid-crystalline properties of both main-chain and side-chain PLCs consisting of various mesogenic moieties. From a technological viewpoint, PLCs have been proposed for various applications including displays, strengthened materials, and optical storage devices, etc. It is well-known that the interesting properties of liquid crystals (LC), low molecular weight LCs and PLCs, arise from a cooperative interaction among mesogens. For PLCs, the inter- and intramolecular interactions between mesogenic moieties may be considered to play an important role in determining the liquid-crystalline properties. Although much research has been conducted on the liquid-crystalline phase behavior of PLCs in the solid state, little attention has been paid to the solution properties of PLCs. It is expected that because of the cooperative interaction among mesogens such properties as the hydrodynamic parameters of the PLC solution are different from those of nonmesogenic polymers in solution. In fact, such a difference has been clearly recognized for poly(methacrylates) with mesogenic methoxycyanobiphenyl side chains.[1] It is useful, therefore, to study the solution properties of PLCs in order to obtain a deeper understanding of the mesogenic interactions.

Among a variety of fluorescent probes detecting hydrophobicity, segment mobility, and so on, excimer-forming chromophores provide information on molecular interaction.[2] A few studies have been reported on excimer formation of fluorophoric mesogens in their liquid-crystalline states.[3,4] Recently, we have reported the kinetics of excimer formation of 4-cyano-4′-alkylbiphenyl compounds in terms of the influence of the morphology of the LC phases on the emission properties.[5] In this paper, we explore the inter- and intramolecular interactions between mesogenic moieties in PLCs in solution by means of fluorescence spectroscopy.

Poly[[(4-cyanobiphenyl-4′-yl)oxy]alkyl acrylate] (PACB*n*; where *n* is the number of methylene units in the spacer, *n* = 2, 3, 5, 6, and 11) and 4-(*n*-pentyloxy)-4′-cyanobiphenyl (5OCB) were used in this study. PACB*n* was prepared by the method reported by Shibaev et al.[6] 5OCB was purchased from Merck Co. and was used without further purification. Molecular weight and thermotropic properties of PACB*n*, determined by gel permeation chromatography and differential scanning calorimetry, respectively, are listed in Table I. PACB*n* and 5OCB were dissolved in tetrahydrofuran (THF), and the solutions were deaerated by several freeze–pump–thaw cycles in a quartz cell.



PACBn

Steady-state fluorescence spectra (corrected) were measured on a Hitachi F-4000 fluorescence spectrometer. Time-resolved fluorescence measurements were performed with a picosecond time-correlated single-photon-counting system, details on which have been reported elsewhere.[7] The instrument response function of the system was 60-ps fwhm. The spectra were not corrected for the wavelength-dependent sensitivity of the photomultiplier used in our system (Hamamatsu R1564U-01). Fluorescence spectra in concentrated solutions were measured by front-face excitation and front-face detection of emission. The temperature of the samples was controlled by means of a calibrated temperature-controlling unit.

Figure 1 shows fluorescence and absorption spectra of PACB3 and 5OCB in THF. In dilute solution (2.7×10^{-6} M), PACB3 showed a fluorescence spectrum with a maximum at 368 nm and a broad shoulder in the longer wavelength region compared to that of 5OCB (3.2×10^{-6} M), while the absorption spectrum of PACB3 was approximately identical with that of 5OCB. On the basis of the similarity of the absorption spectra, the broad shoulder of PACB3 may imply some contribution of excimer emission. It was found that in dilute solutions the fluorescence intensity at around 420 nm in the normalized spectra increased in the order of 5OCB ~ PACB11 < PACB2 ~ PACB5 ~ PACB6 < PACB3. This may be a consequence of the intramolecular excimer formation: the cyanobiphenyl (CB) chromophores of PACB11 are effectively isolated from each other due to decoupling of the CB moieties from the main chain, behaving like 5OCB; on the other hand, the CB moieties in PACB3 may have favorable distribution for the excimer formation. However, in PACB2, because of a short spacer the CB mesogens are coupled rather strongly with the main chain and their mobility is strongly limited as evidenced by the CPK model of this polymer. The less effective excimer formation in PACB2 can be explained by the unfavorable orientation and the limited mobility of the CB mesogens in this polymer. In Figure 1 is also included an emission spectrum of the concentrated solution of PACB3 (1 M in THF). It is evident that in the concentrated solution PACB3 showed a spectrum with a maximum at a longer wavelength than that of the dilute solution.

The decay behavior of the monomer and excimer emissions of PACB*n* in both dilute and concentrated solutions was measured with a picosecond time-correlated single-photon-counting system. It was shown that the decays could be analyzed by a triple-exponential function in the form of $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$ as judged by reduced χ^2 and Durbin–Watson (DW) parameters. A double-exponential function was examined but gave a poorer fit. In the dilute solutions the monomer emissions were associated with a fast-decaying component (τ_1 = 50–100 ps), a component with lifetimes τ_2 of 700–1100 ps, and a slowly decaying component (τ_3 = 5–6 ns), while in the excimer emissions were observed components with lifetimes τ_1 of 50–100 ps, τ_2 of 400–1000 ps, and τ_3 of 4–6 ns. It is noted that no rise component was observed in any samples in dilute solutions when monitored at the excimer emissions (450 nm), indicating that the excimer formation in the dilute solutions may be too fast to be detectable with our apparatus. In concentrated solutions,

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Table I
Thermodynamic Properties of PACB*n*

n	M_n	T_c, °C	T_g, °C	ΔH_c, J/mol	ΔS_c, J/mol·K
2	3800	98	66	322	0.87
3	4200	72	48	31	0.09
5	4600	77	42	100	0.28
6	4800	104	24	800	2.12
11[a]	5000	115	5	3300	8.51

[a] LC phase, smectic. PACB*n* with *n* = 2, 3, 5, and 6 showed only the nematic phase.

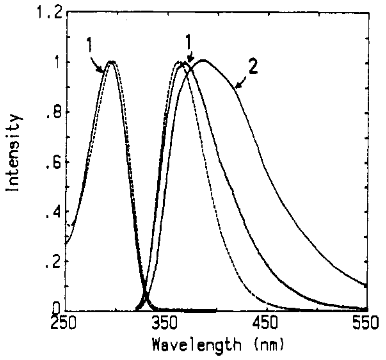

Figure 1. Absorption and fluorescence spectra (normalized) of PACB3 (—, curves 1 and 2) and 5OCB (···, dilute) in THF. Excitation at 300 nm. (1) PACB3 in dilute solution. (2) PACB3 in concentrated solution.

the monomer emissions were associated with a fast-decaying component (τ_1 = 100–200 ps), a component with lifetimes τ_2 of 500–600 ps, and a slowly decaying component (τ_3 = 6–7 ns), whereas in the excimer emissions were observed components with lifetimes τ_1 of 10–50 ps (negative A_1), τ_2 of 800–1500 ps, and τ_3 of 7–10 ns. Contrary to the results in dilute solutions, a rise component was observed in the excimer emissions (τ_1 with negative A_1; 450 nm).

Figure 2 shows the time-resolved fluorescence spectra of PACB3 obtained in the dilute and the concentrated solutions. For the dilute solution, the emission spectrum with a maximum at around 360 nm was observed at t = 0 and the shape of the spectrum scarcely changed with time. On the other hand, the concentrated solution showed red-shifted emission with a maximum at around 400 nm immediately after pulse excitation, which was followed by a shift of the maximum to longer wavelength. This result strongly suggests that two excimer species exist in the concentrated solution.

The occurrence of aggregates in side-chain PLCs in solution was reported by Springer and Weigelt.[8,9] They suggested that the backbone tacticity may influence the aggregation process. More recently, Duran and Strazielle studied the solution properties of PLCs with methoxybiphenyl side groups through oligo(ethylene oxide) spacers and reported a strong tendency toward formation of aggregates in solution owing to the biphenyl–biphenyl interaction.[1]

It seems reasonable to assume that the interaction between the mesogenic biphenyls in PACB3 is strong enough to form aggregates in solution. The excimer emission observed at t = 0 in concentrated solution may be due to an intermolecular excimer with head-to-tail configuration by the analogy of the case of 4-(octyloxy)-4′-cyanobiphenyl (8OCB), in which the excimer conformation was reportedly head-to-tail owing to the formation of an intramolecular charge-transfer (CT) complex.[3] Although the origin of the low-energy excimer observed in the time-resolved spectra of the concentrated solution is not fully understood at the present time, it might be due to an excited complex composed of more than two CB chromophores as a terplex. The interaction between the mesogenic groups may play an important role for the occurrence of the liquid-crystalline state as well as the formation of aggregates in solution. Detailed studies on this subject are now in progress and will be reported later.

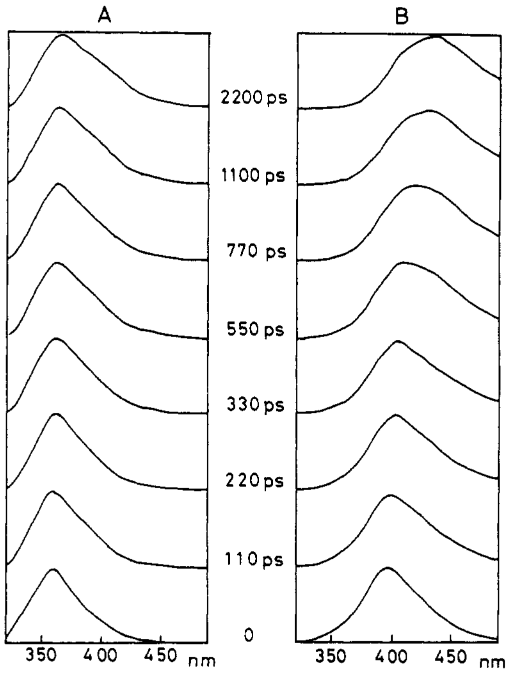

Figure 2. Time-resolved normalized fluorescence spectra of dilute (A) and concentrated (B) solutions of PACB3 in THF. The number in the figure denotes the delay times after pulse excitation. Excitation at 310 nm.

References and Notes

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