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Excimer Formation in Main-Chain Polymer Liquid Crystals with Mesogenic *p*-Phenylenediacrylic Acids

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ABSTRACT: Polyesters of *p*-phenylenediacrylic acid (PDA) and various ethylene glycol derivatives (di-, tri-, tetra-, and penta-) have been found to exhibit liquid-crystalline (LC) behavior. Annealing of the polymer liquid crystals (PLC) at LC temperatures was essential for PLC to form a LC phase, and the ethylene glycol spacers strongly affected growth of the LC phase. Structure of the LC phase seemed to be different among the PLCs as evidenced by the thermodynamic data of the PLCs. Excimer formation behavior of PLCs was investigated by both steady-state and time-resolved measurements of fluorescence with the aid of a picosecond single-photon-counting system. Excimer was found to be formed much more effectively in the LC state than in the isotropic state of PLCs, due to parallel orientation of the chromophores in the LC state. Time-resolved measurements revealed that excimer formation resulted mainly from excitation of preformed chromophore pairs in the ground state. Lifetimes of excimer were found to be longer in a more ordered system due to restricted mobility of the PDA chromophores in such a system.

Introduction

Polymer liquid crystals (PLC) have become of interest in recent years from both scientific and industrial points of view. Early studies on the PLCs were concentrated on lyotropic PLCs such as tobacco mosaic viruses dispersed in aqueous solutions[1] and polypeptides in organic solutions.[2] Research activity in this area has recently increased, since the discovery of the preparation of ultrahigh-strength fibers by spinning of aromatic polyamides from anisotropic (lyotropic) solutions.[3] The importance of the liquid-crystalline state for the preparation of uniaxially oriented polymeric structures of ultrahigh modulus and strength has been realized.[3] The shortcomings of the lyotropic liquid-crystalline states for this purpose are evident. Solvents, necessary for the formation of the lyotropic liquid crystals, must be removed after spinning or molding. This stimulated the development of a process for formation of fibers from liquid-crystalline melts (thermotropic PLCs).[3] The technology of thermotropic PLCs commenced with the discovery of thermotropic copolyesters prepared from poly(ethylene terephthalate) and *p*-hydroxybenzoic acid.[4] Since then, many studies have been performed on thermotropic PLCs and, in particular, on those with main-chain mesogenic groups.[5]

In an earlier paper, we reported topochemical photodimerization in thermotropic main-chain PLCs with mesogenic *p*-phenylenediacrylic acid (PDA) moieties as a possible approach to two-dimensionally reinforced polymer materials.[6] We demonstrated that polyesters having PDA moieties and diethylene glycol as flexible spacers showed nematic behavior. In the temperature range where the polyesters exhibited liquid-crystalline (LC) phase behavior, the efficiency of the photodimerization leading to the formation of interchain cross-linking was significantly higher. This was interpreted in terms of a favored orientation of the photoreactive PDA moieties in the LC phase.[6]

Detailed studies on the photodimerization behavior of a polyester having the PDA chromophore were reported by Reiser et al.[7] Their sample was a polyester composed of the PDA unit and 1,4-bis(2-hydroxyethoxy)cyclohexane. Unlike our polyesters described above, their polyester did not show LC behavior; however the PDA chromophores reportedly tended to associate and ~25% of the PDA chromophores existed as a pair in the ground state.[8,9] They further investigated the emission properties of the polyester and found that excimer was formed predominantly from the paired state of the PDA chromophores; thus, excimer formation was extremely fast.[8,9]

Polyesters composed of the PDA chromophores and various ethylene glycol derivatives exhibit LC behavior, and it was expected that they would show emissive properties different from those of amorphous polymers. In this paper, we study the LC behavior and the emissive properties of the polyesters composed of PDA chromophores and ethylene glycol spacers, and we discuss their fluorescence behavior in relation to the morphology of the polymers. In particular, we explore the time-rsolved fluorescence decay profiles of these systems with the aid of a picosecond single-photon-counting system.

Experimental Section

The structures of the polymers used in this study as well as their abbreviations are shown in Figure 1. *p*-Phenylenediacrylic acid (PDA) and its ethyl ester (Et_2PDA) were synthesized as reported previously.[6,10] Polycondensation of Et_2PDA with various ethylene glycols (di-, tri-, tetra-, and pentaethylene glycols) was performed by the method reported by Iwata et al.[10]

Characterization. The number-average molecular weight (M_n) of the polyesters was determined by gel permeation chromatography (GPC) calibrated with standard polystyrene samples. GPC was also employed for the fractionation of the polymers. LC and phase-transition behaviors were observed with an Olympus Model BHSP polarizing microscope equipped with a Mettler hot-stage Model FP-80 and FP-82. Thermodynamic data were obtained with a differential scanning calorimeter (SEIKO I&E SSC-5000) at a heating rate of 10 °C/min.

Polymer films were prepared by casting the polymer solution in chloroform onto glass plates, followed by evaporation of the solvent under reduced pressure. After drying completely, the films were annealed in a thermostat at temperatures where the polymers exhibited the LC behavior. Annealing was essential to form the LC phase over the whole area of the PLC films.

Fluorescence Measurements. Steady-state fluorescence

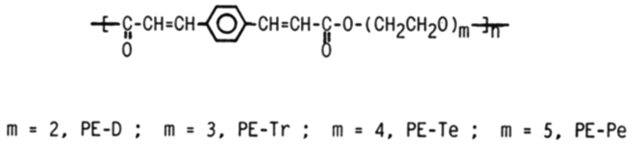

Figure 1. Structure of PLCs used in this study and their abbreviations.

spectra were measured on a Hitachi F-4000 fluorescence spectrometer.

Time-resolved fluorescence measurements were performed with a picosecond time-correlated single-photon-counting system, the details of which have been reported elsewhere.[11] Briefly, a synchronously pumped, cavity-dumped dye laser (Spectra Physics 375B and 344S) operated with a mode-locked Nd:YAG laser (Spectra Physics 3460 and 3240) was an excitation pulse source with a pulse width of 4 ps (fwhm). We obtained a frequency-doubled pulse for the excitation of the samples through a KDP crystal (Inrad 531). Fluorescence from the samples was detected at right angles to the excitation pulse through a monochromator (Jasco CT-25C) with a microchannel-plate photomultiplier (Hamamatsu R1564U-01). Signals from the photomultiplier were amplified (HP 8447D), discriminated (Ortec 583), and used as a stop pulse for a time-to-amplitude converter (TAC; Ortec 457). A start pulse was provided from a fast photodiode (Antel AR-S2) monitoring a laser pulse through a discriminator (Ortec 436). Data were stored in a multichannel analyzer (Canberra 35 Plus) and then transferred to a microcomputer (NEC 9801) where decay analysis was performed by an iterative nonlinear least-squares method.[11] The instrument response function of the whole system was 60-ps fwhm.

In the fluorescence measurements on PLC films and on concentrated solutions, optical alignment of front-face excitation and front-face measurement of emission were employed.

The temperature of the samples was controlled by means of a Jasco HTV cell coupled with a temperature-controlling unit.

1,2-Dichloroethane used in the fluorescence measurements was of spectroscopic grade and was used without further purification. All fluorescence measurements were performed in the presence of air.

Results and Discussion

Thermotropic Properties of Polymers. Annealing of the polyesters at LC temperatures was quite important for the polyesters to exhibit LC behavior over the whole area of the films. Figure 2 shows the effect of annealing of the PE–Te film on the growth of the LC phase. Annealing was performed at 46 °C, which corresponds to the reduced temperature, T_{red} $(=T/T_{\mathrm{C}})$, of 0.95. Photographs of the observed textures were taken at appropriate time intervals with a pair of crossed polarizers. Immediately after the PE–Te film was prepared, the whole film was in an amorphous state and no texture was observed. With time, the LC domains grew as shown in Figure 2 (a and b). The whole film showed the LC phase after 170 h (Figure 2c).

In Figure 3, the fraction of the LC domain is plotted as a function of annealing time. Annealing was performed at $T_{\mathrm{red}} = 0.95$. As shown below, the phase-transition temperatures (T_{C}) of the samples were different depending on structure of the flexible spacer, and the annealing temperature was varied for each sample. The fraction of the LC domain was determined in the following way. The PLC sample was placed in the Mettler hot stage, the temperature inside was adjusted to $T_{\mathrm{red}} = 0.95$, and the texture of the sample was observed in the polarizing microscope. The transmitted light intensity (I_{t}) was measured with a photodiode as a function of time. Thus, if the sample is amorphous, $I_{\mathrm{t}} = 0$. As the LC phase grows, I_{t} increases and eventually saturates when the whole sample is in the LC phase. The transmitted light intensity at this stage is taken as I_{∞}, and the ratio $I_{\mathrm{t}}/I_{\infty}$ can be regarded as a measure for the fraction of the LC phase exhibited by the PLC sample. In the case where the LC domains were composed of large textures, this method gave less reliable values. In such cases, photographs of the textures were taken in many places in the sample and the areas of the LC domains was measured.

Figure 3 indicates that in PE–D the LC phase grows quite rapidly. Within 20 min it has spread through the whole film. With increasing spacer length between the PDA moieties, the growth of the LC phase slows down. Nearly 7 days were required for the whole PE–Te film to show the LC phase.

Figure 4 shows the glass transition temperature (T_{g}) and the phase-transition temperature (T_{C}) of the PLC samples as a function of molecular weight (M_{n}). It is clearly seen that T_{g} of the PLC samples decreases with increasing spacer length (PE–D >PE–Tr > PE–Te), while T_{C} does not show monotonous variation. Samples with even-numbered ethylene glycol spacers show rather low values of T_{C}, whereas those with odd-numbered ethylene glycol spacers exhibit higher T_{C} values. This phe-

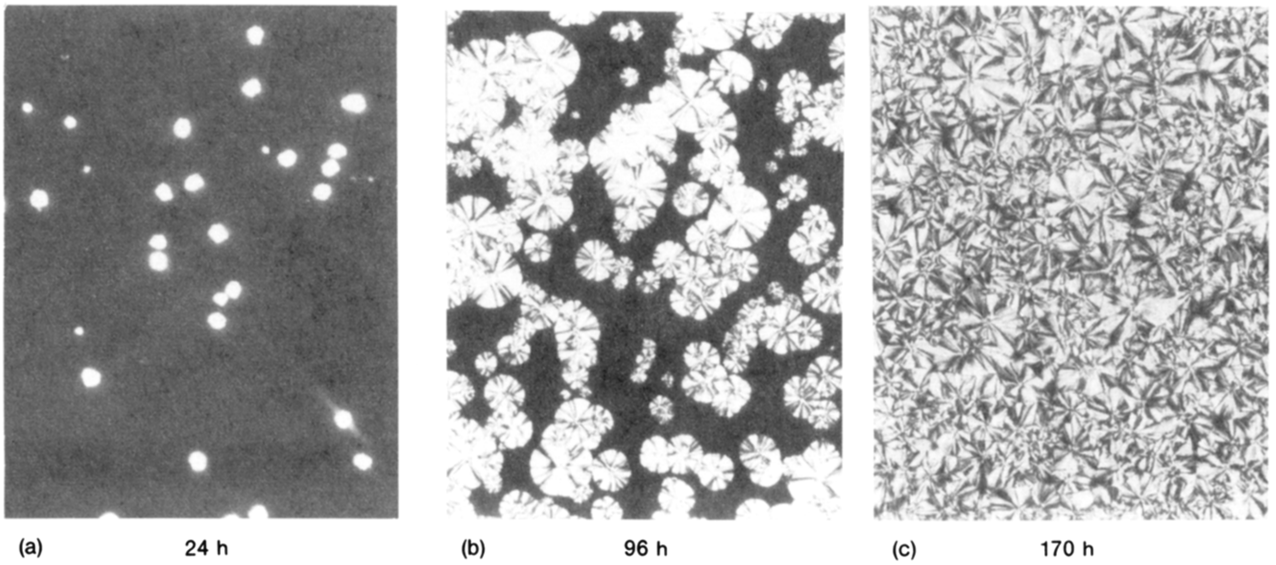
(a) 24 h (b) 96 h (c) 170 h

Figure 2. Effect of annealing of PE–Te film on growth of LC phase. Texture observed in the polarizing microscope is shown: (a) 24 h; (b) 96 h; (c) 170 h. Annealing was performed at $T_{\mathrm{red}} = 0.95$ (46 °C).

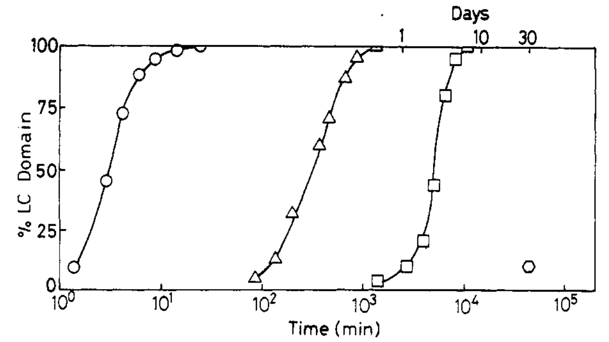

Figure 3. Fraction of LC domains as a function of annealing time: (○) PE-D; (△) PE-Tr; (□) PE-T); (◇) PE-Pe. Annealing was performed at $T_{\rm red}$ = 0.95.

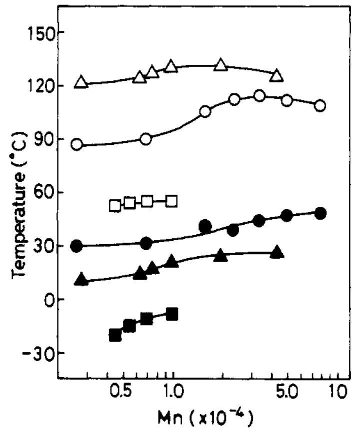

Figure 4. Phase-transition behaviors of polyesters as a function of molecular weight. PE-D: (●) T_g; (○) T_C. PE-Tr: (▲) T_g; (△) T_C. PE-Te: (■) T_g; (□) T_C.

nomenon may be interpreted in terms of odd-even effect commonly observed in LC systems.[12,13] In Figure 5, thermodynamic data on the phase transition of the polymers (ΔH_C and ΔS_C) are shown as a function of M_n. One can see that both ΔH_C and ΔS_C of PE-D are quite low compared with those of PE-Tr and PE-Te. In PE-D, both ΔH_C and ΔS_C are independent of M_n. In PE-Tr and PE-Te, both ΔH_C and ΔS_C increase with increasing M_n up to $\sim 10^4$ and then decrease at higher values of M_n.

Emission Properties of PLC. Et$_2$PDA was used as a model compound of the polyesters containing PDA moieties in the main chain. In dilute solution in 1,2-dichloroethane, Et$_2$PDA showed a structured fluorescence with maximum wavelength at 370 nm (Figure 6a).[8,9] With increasing the concentration of Et$_2$PDA, the fluorescence intensity at 370 nm decreased and a new peak maximum wavelength at 470 nm appeared.[8,9] It is well-known that PDA derivatives form excimer,[8,9] consequently we can assign the peak at 370 nm to monomer emission (I_M) and the peak at 470 nm to excimer emission (I_E).[8,9] In fact, the concentrated solution of Et$_2$PDA (2 M) showed exclusively excimer emission.

The polyester films showed both monomer and excimer emissions. One example is shown in Figure 6c. One can see that excimer emission is predominant in this sample. As a measure for efficiency of the excimer formation in the PLCs, we took the ratio of I_E/I_M, fluorescence intensities at 470 nm and at 370 nm, respectively.

The temperature dependence of the ratio of I_E/I_M is shown in Figure 7 where ln (I_E/I_M) is plotted as a function of the reciprocal of the absolute temperature. Since we were aware of the importance of the thermal history applied to the PLC samples, we measured the fluorescence spectra of the samples under the same condition. Namely, the PLC films were subjected to annealing at $T_{\rm red}$ = 0.95 until the whole film showed the LC phase. The samples were then cooled slowly to a temperature where the fluorescence measurement started. The temperature of the sample was then raised at a rate of 1 °C/min over the phase-transition temperature (indicated by an arrow in each plot in Figure 7) to a temperature higher by 40–60 °C than the T_C of the sample. Thereafter, the sample was kept at this temperature for 30 min and then cooled at a rate of 1 °C/min. In Figure 7, the ratios of I_E/I_M determined in the course of heating are indicated by ○ and those of the cooling process are depicted by △.

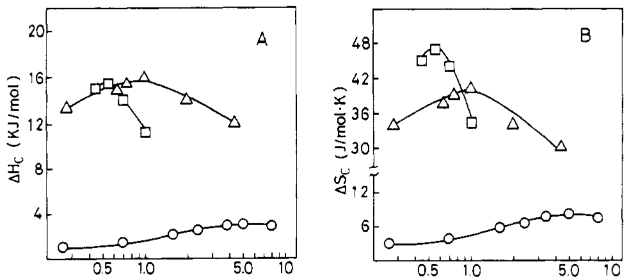

Figure 5. Thermodynamic data on phase transition of polyesters as a function of molecular weight: A, ΔH_C; B, ΔS_C; (○) PE-D; (△) PE-Tr; (□) PE-Te.

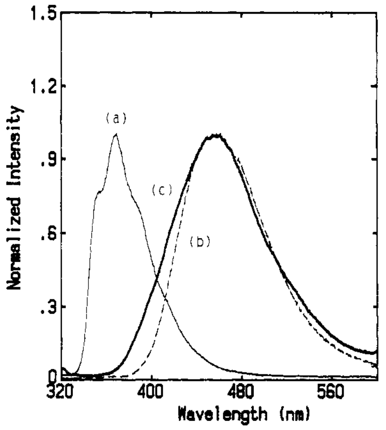

Figure 6. Fluorescence spectra of Et$_2$PDA in 1,2-dichloroethane and PE-D film in the presence of air: (a) 1×10^{-5} M Et$_2$PDA; (b) 2 M Et$_2$PDA; (c) PE-D film. λ_{ex} = 310 nm.

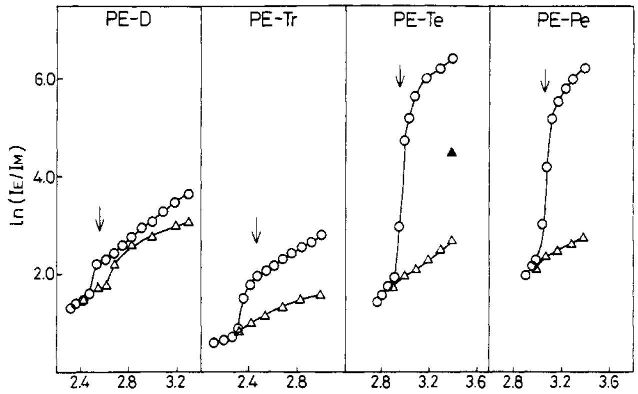

Figure 7. Arrhenius-type plots for the ratio of the fluorescence intensity at 470 nm to that at 370 nm, I_E/I_M. (○) In the course of heating; (△) in the course of cooling. Heating and cooling rates 1 °C/min. Arrows in the figures indicate T_C of PLCs. (▲) I_E/I_M value after 4 days of annealing (see text).

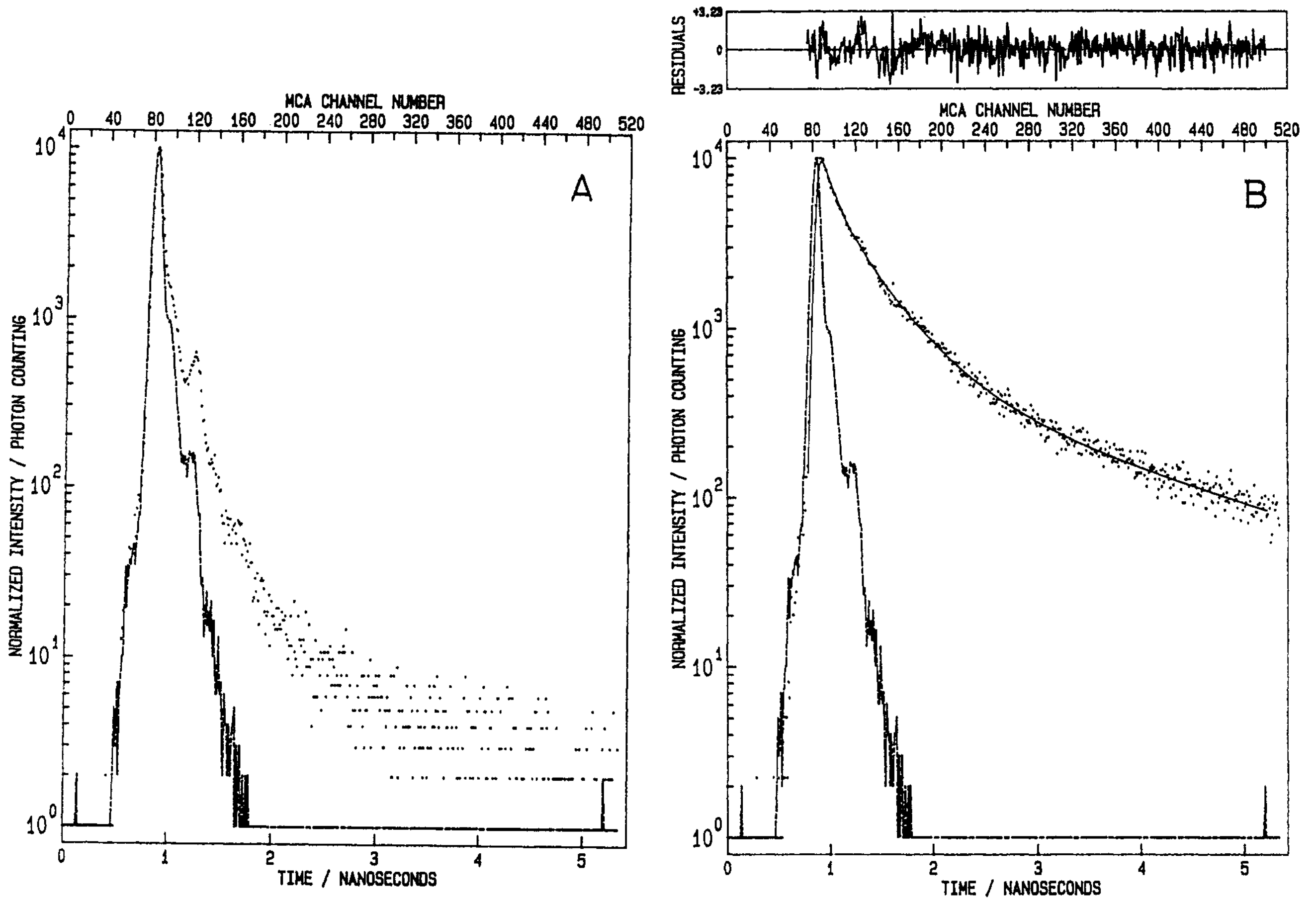

Figure 8. Fluorescence decay profiles of PE–D monitored at 370 (A) and 470 nm (B). The instrument response function (fwhm ~60 ps) is also shown in (A) and (B), and the fitting curve is included in (B).

Figure 7 demonstrates a characteristic feature on the emissive properties of the PLCs that indicates excimer is formed with high efficiency in the LC state, and an abrupt drop in the ratio of I_E/I_M is observed at a temperature close to T_C of every sample. This is in good accord with our interpretation in terms of the spatial orientation adopted by the PDA chromophores in PLCs. In the LC state, the PDA chromophores are aligned parallel to each other, and the face-to-face configuration of the chromophores, essential to the formation of excimers, is easily obtainable. It is, therefore, quite reasonable that excimer is formed effectively in the LC state.

Another characteristic feature seen in Figure 7 is that in PE–D both the heating curve and the cooling curve showed a similar temperature profile while in other polyesters the cooling curves were different from the heating curves. In other words, in PEt–Tr, PE–Te, and PE–Pe no abrupt change in I_E/I_M was observed at T_C in the cooling curves. This phenomenon is interpreted in terms of the slow formation of the LC domains in these PLCs as shown in Figure 3. Under the experimental condition where the Arrhenius-type plots were constructed in the course of cooling, time was by no means sufficient for these PLCs to form the LC phase. Thus, the I_E/I_M values observed in these PLCs below T_C should be regarded as those of the isotropic states. After the measurements were over, the PE–Te film was left at 25 °C for 4 days and the fluorescence spectra were taken. The I_E/I_M value was found to be hgher than the previous one as indicated in Figure 7, which supports the above view.

Figure 8 shows fluorescence decay profiles of PE–D monitored at 370 nm (monomer emission) and at 470 nm (excimer emission) as a typical example of the time-resolved fluorescence decay analysis. The temperature was 90 °C where PE–D showed the LC phase. It is clearly seen that the decay of the monomer fluorescence is fast and shows a profile similar to the instrument response function (~60-ps fwhm). In addition to the fast-decaying species, a slowly decaying species can be seen in the monomer fluorescence, although the slow species is only a minor component. However, origin of this slow species is obscure. It is not certain whether it arose from the dissociation of the excimer or simply from contamination of the monomer emission with the excimer emission because of the unresolved nature of the monomer and excimer emissions of the present system (Figure 6).

Because of the fast decay of the monomer emission, fitting of the decay curves with a function of $\sum A_i e^{-t/\tau_i}$ was difficult, giving unreliable values of the lifetimes as judged by χ^2 and Durbin–Watson (DW) parameters. For example, the best fitting of the decay curve shown in Figure 8a gave the results of $A_1 = 0.5484$, $\tau_1 = 9.9$ ps, $A_2 = 0.005\,48$, $\tau_2 = 240$ ps, $A_3 = 0.000\,063$, and $\tau_3 = 2550$ ps; however, fitting itself was very poor: $\chi^2 = 4.80$ and DW = 0.31. Although the absolute values of the lifetimes of the monomer emission are not reliable, it is certain that the decay of the monomer emission is fast.

Unlike the monomer emission, the excimer emission can be analyzed satisfactorily with double- or triple-exponential functions irrespective of the kind of PLCs and the temperature. Fitting of the decay curve shown in Figure 8b, for example, gave the results of $A_1 = 0.017\,01$, $\tau_1 = 80.2$ ps, $A_2 = 0.008\,76$, $\tau_2 = 473$ ps, $A_3 = 0.001\,311$, $\tau_3 = 2530$ ps with $\chi^2 = 1.0265$, and DW = 1.989. Thus, our discussion is limited to the decay profiles of the excimer emissions.

In Figure 9 are shown the lifetimes of the excimer emission as a function of temperature. Note that no rise com-

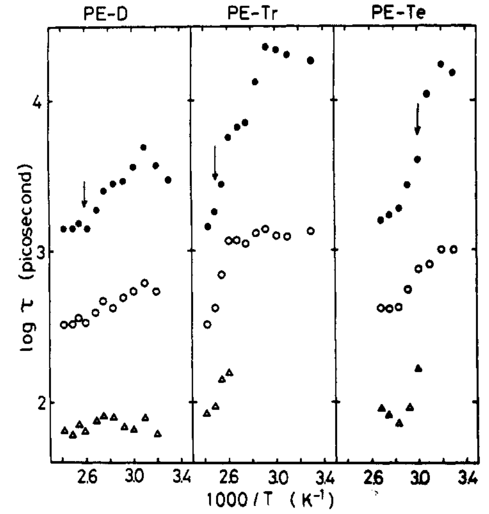

Figure 9. Lifetimes of excimer emission of PLCs as a function of temperature: (△) τ_1; (○) τ_2; (●) τ_3 ($\tau_1 < \tau_2 < \tau_3$). Arrows in the figures indicate T_C of PLCs.

ponent was obtained at any temperature on any samples. This means that the excimer formation is too fast to be detectable with our apparatus or excimer is formed by the excitation of paired chromophores. In this regard, Reiser et al. investigated the emission properties of a polyester (PPDA) composed of PPDA and 1,4-bis(2-hydroxyethoxy)cyclohexane.[8,9] The monomer emission of PPDA in 1,2-dichloroethane solution was found to be very short-lived (lifetime ~80 ps) while the excimer emission was described by a double-exponential function with $\tau_1 \sim 80$ ps and $\tau_2 \sim 5000$ ps.[8,9] They inferred that the excimer was not formed by the usual bimolecular quenching but arose through the excitation of paired chromophores formed in solution. Even in solution, the PDA chromophores have a strong tendency to aggregate in the ground state; thus, it is reasonably assumed that the PDA chromophores exist almost exclusively as a pair in the LC state. Consequently, excimer may be formed in the present system by the excitation of the preformed chromophore pairs, which is in good agreement with the absence of the rise component in the excimer emission.

With respect to the three lifetimes associated with the excimer emission, τ_1 (△), τ_2 (○), τ_3 (●) ($\tau_1 < \tau_2 < \tau_3$), both PE–Tr and PE–Te have longer values than PE–D in the LC state, although the lifetimes in the isotropic temperature region are similar to each other (T_C is indicated in the figure by an arrow). This trend can be most clearly seen in the longest component: τ_3 of PE–Tr and PE–Te in the LC temperature region is considerably longer than that of PE–D. This may be related to the thermodynamic parameters of the PLCs (Figure 5). According to Flory and Ronca, ΔS is proportional to the second power of the order parameter (S) of the system;[14] thus, ΔS can be used as a measure of the order parameter. Parallel tendency between ΔS and S can be rationalized if we assume that PLCs have the same values of entropy in the isotropic state. Namely, a large value of ΔS means a small value of entropy in the LC state, thus higher orientational ordering in the LC state. Such a parallel relationship has been already reported for main-chain PLCs,[15,16] side-chain PLC,[17] and low MW liquid crystals.[18] Lower values of ΔS_C of PE–D indicate that PE–D has a much less ordered structure in the LC state than PE–Tr and PE–Te. The disordered structure of the LC state of PE–D may lead to high mobility of mesogenic chromophores in the LC state; thus, a bimolecular quenching process leading to a shorter lifetime may be facilitated. On the other hand, in PE–Tr and PE–Te the structure of the LC state is highly ordered; thus, mobility of the chromophores is restricted, leading to a slow nonradiative decay of the excited state and a longer lifetime. The large drop of lifetimes near the phase-transition temperature can be interpreted on the same basis. Mobility of the mesogenic chromophores is much higher in the isotropic state than in the LC state; thus, lifetimes in the isotropic state are reasonably shorter than those in the LC state. Furthermore, order of the isotropic state is similar as assumed above (the same value of entropy), and the mobility of the chromophores is similar in the isotropic state; therefore, lifetimes of the excimer are similar among PLCs.

Conclusions

Excimer formation in polyesters having in-chain PDA chromophores was studied in connection with their LC behavior by both steady-state and time-resolved measurements of fluorescence. Results may be summarized as follows. (1) The rate of LC phase formation is strongly affected by the spacer length between PDA chromophores and is highest in PE–D. (2) The structure of the LC phase is different as evidenced by the thermodynamic data, and PE–D seems to have a less ordered structure than PE–Tr and PE–Te. (3) Excimers are formed much more effectively in the LC state than in the isotropic state, because of the parallel orientation of the chromophores in the LC state. (4) Excimers are presumably formed from preformed chromophore pairs. (5) Lifetimes of the excimers are longer in the more ordered systems because of the restricted mobility of the relevant chromophores. excimer formation behavior has been interpreted on the basis of the morphology of the system.

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Registry No. PE-D (copolymer), 124921-54-6; PE-D (SRU), 117371-39-8; PE-Tr (copolymer), 124921-55-7; PE-Tr (SRU), 99763-64-1; PE-Te (copolymer), 124921-56-8; PE-Te (SRU), 101949-80-8; PE-Pe (copolymer), 124921-57-9; PE-Pe (SRU), 101949-79-5.