Roles of Composition Heterogeneity on Ordering of a Liquid Crystalline Copolyester: Nematic/Nematic Biphase and Nonequilibrium Pattern Formed by Seeded Growth of LC Domains

Toshio Shiwaku,[†] **Akemi Nakai,**[‡] **Wei Wang,**[§] **and Takeji Hashimoto***[,‖]

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Kyoto 615-8510, Japan

Received January 8, 2005; Revised Manuscript Received October 1, 2005

ABSTRACT: Roles of composition heterogeneity on pattern formation via phase separation and ordering of a main-chain type liquid crystalline (LC) copolyester have been investigated in a wide range of temperature. For this purpose, as-cast films of the neat LC copolyester having optically homogeneous and isotropic property, as a trapped nonequilibrium initial state, were first prepared by solvent casting. Ordering process of the copolyester films induced by isothermal annealing of the as-cast films at various temperatures was observed in situ and at real time under polarized optical microscopy. Upon increasing temperature T, we found new phases of N (nematic) single phase and N/N biphase in which nematic domains having high and low order parameters coexist, within the phase previously assigned as the semicrystalline phase. The N single and N/N biphase exist between the semicrystalline phase and N/I (isotropic) biphase in which nematic domains coexist with optically isotropic domains. In addition to this equilibrium or at least *pseudo*-equilibrium patterns, various interesting nonequilibrium textures were observed by first applying isothermal annealing to the specimen at various temperatures in the N/I biphase or in isotropic single phase (I) for a range of time, followed by quenching of it to room temperature. The textures observed are as follows; (i) "dendritic anisotropic LC texture" grown epitaxially toward isotropic matrix from the interface of preexisting anisotropic domains which were developed in the first isothermal annealing process and (ii) impurities-induced nonequilibrium Schlieren texture with disclination lines having strength $s = +1$ with $\phi = \pi/2$ rather than thermodynamically more stable $s = \pm{}^1/_2$, which is grown in the matrix phase from interfaces of preexisting small and spatially isolated round anisotropic domains. The preexisting domains act as seeds for the growth of the nematic domains whose directors tangentially orient around the seeds. The former nonequilibrium texture (i) is a consequence of a concentration gradient of molecular species having high mesogenic groups being created in the periphery of the preexisting anisotropic domains. The average concentration of the mesogenic group is expected to decrease with a distance from the interface of the anisotropic domains, and this concentration gradient is responsible for the epitaxial growth of LC phase. The later nonequilibrium texture (ii) reveals also the epitaxial growth in a sense that the interface of anisotropic domains, which are isolated and round in the isotropic matrix, acts as wedge disclination centers and controls energetically unfavorable orientation of directors of nematic liquids, when isotropic-to-nematic phase transition occurs in the isotropic matrix during the cooling process after the first annealing process.

I. Introduction

Thermotropic liquid crystalline (LC) polymers are now widely used as a high-performance resin because of their superior mechanical, thermal, and rheological properties. Many of commercial LC polymers are aromatic copolyesters having 4-hydroxybenzoic acid (HBA) group as a mesogenic unit. These copolyesters, especially those based upon HBA and ethylene terephthalate (ET) units, often exhibit compositional heterogeneities in monomer formulations among molecules and/or statistical heterogeneity in monomer sequence along backbone chains. The composition heterogeneity in the primary structure of the neat LC copolyesters, which is usually originated from the difference in reactivity among monomers on the polymerization processes,[1−5] inevitably introduces self-assembled structures, having spatial fluctuations in HBA concentration or phase separation between HBA-rich and ET-rich components in as-polymerized or once-processed LC copolyesters.[1−4,6−8] In this sense, the behavior of the neat copolyester may be superficially considered to be similar to a binary mixture polymer blend. However, in reality, in many aspects we realize that the phase separation induced by the composition heterogeneity for the neat copolyesters is fundamentally different from the conventional binary blends, as will be highlighted later in section IV-2.

In the previous study,[9] we explored the kinetics of pattern formation of a neat LC copolyester having a bimodal composition distribution by using the solvent-cast film having optically homogeneous and isotropic property as an initial state of specimens. We elucidated ordering kinetics of the specimens during isothermal annealing process induced by temperature−jump (T−jump) from the glassy state at room temperature to various temperatures. The ordering process of the copolyester films was observed in situ and at real time under polarized optical microscopy (PLM). The patterns formed in the films changed with increasing tempera-

---

[*] To whom correspondence should be addressed.

[†] Present address: Polyplastics Co. Ltd., Research & Development Center, 973 Miyajima, Fuji 416-8533, Japan.

[‡] Present address: Department Home Economics, Kyushu Woman's University, 1-1 Jiyugaoka, Yawata-nishi-ku, Kitakyushu 807-8586, Japan.

[§] Present address: State Key Laboratory of Functional Polymer Materials for Adsorption and Separation and Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, P. R. China.

[‖] Present address: Advanced Science Research Center, Japan Atomic Energy Agency, Tokai-mura, Ibaraki Prefecture, 319-1195, Japan.

10.1021/ma050042d CCC: $30.25 © 2005 American Chemical Society
Published on Web 11/23/2005

ture from semicrystalline phase, nematic, and isotropic biphase (N/I) in which nematic phase and isotropic phase coexisted due to phase separation between the rigid and flexible molecular species in the neat copolyester, and isotropic single phase (I). In that work, we focused on time evolution on pattern formation during isothermal phase-separation process in the N/I biphasic temperature region. We elucidated that the kinetics of the phase separation at given temperatures driven by the composition heterogeneity of the neat LC copolyester was apparently identical to that of the physically blended systems comprised of the LC copolyesters and isotropic melts of poly(ethylene terephthalate).[10,11]

In this work, we use the same copolyester as that used in the previous study[9] and focus further on the roles of the composition heterogeneity of HBA on the pattern formation in general, other than the phase separation kinetics in the N/I biphasic region.[9] For this purpose, we carefully vary heat treatment conditions in a wide range of temperature with a small temperature increment. In this paper we shall report two kinds of patterns that were newly found for this neat LC copolyester under the isothermal and nonisothermal heat treatment conditions.

Under prolonged isothermal annealing conditions, we discovered equilibrium or at least *pseudo*-equilibrium nematic single phase (N) pattern and nematic−nematic biphase (N/N). The N/N pattern in which two nematic phases having high and low order parameters coexist appeared over a narrow temperature range. Because of its quite narrow temperature range and slow ordering process we could not identify the N/N biphasic pattern in the previous work.[9] First of all, the N/N biphase found for the neat copolyester itself is a quite interesting phenomenon. Moreover the observed trend of transformation from N single phase to N/N biphase with increasing temperature seems to be also an interesting phenomenon in a sense that the trend may not be able to be easily explained for binary N/N polymer mixtures. We think that these phenomena are not trivial at all but rather fundamentally important for self-assembly of copolymers having composition heterogeneities, as will be discussed later in section IV-1.

Other unique patterns observed under nonisothermal annealing conditions were nonequilibrium patterns such as follows: (i) “dendritic anisotropic LC texture” and (ii) “impurities-induced” Schlieren texture having strength $s = +1$ with $\phi = \pi/2$ having tangentially oriented directors around preexisting, round, and isolated anisotropic domains, as will be detailed later in the text (section IV-3). Note that this texture is thermodynamically unfavorable compared with the texture having $s = \pm^1/_2$.

The bimodal composition heterogeneity played an important role to generate these unique structures of the neat LC copolyester. We will present a full description of the pattern formation of the LC copolyester, which will give possibilities to design the structure for improved performances of commercial LC copolyesters.

II. Experimental Section

The polymer used is a liquid crystalline (LC) copolyester synthesized by a step polymerization with 50 mol % of 4-hydroxybenoic acid (HBA) and 50 mol % of ethylene terephthalate units (ET) according to the conditions reported in ref 5. The characterization of the composition heterogeneity was described in detail in Appendix I in the previous report.[9] Here, we only state the outline of the compositional analysis for the LC copolyester. It was carried out with high performance liquid chromatography (HPLC) with eluent of a mixture of chloroform/hexafluoro-2-propanol (HFIP)/acetic acid (100/5/3 in volume). A separation column used was ERC-silica-2122 (8 mm in diameter, 250 mm in length) provided by Perkin-Elmer, Inc. The sample polymer was dissolved in a mixture of chloroform/HFIP (9/1 in volume), filtered with 0.5 μm of pore size PTFE filter, and then injected to HPLC. The compositional profile was monitored with ultraviolet at 254 nm.

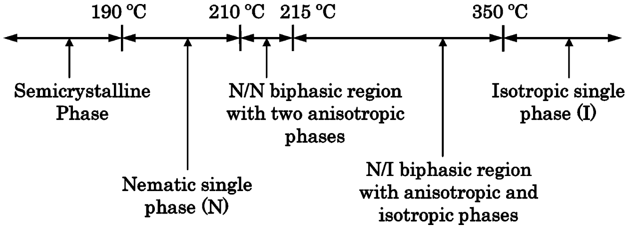

Figure 1. Various phases of the LC copolyester observed on the ordering process of the as-cast films with the isothermal heat-treatment at various temperaures.

To obtain the as-cast film specimen, the LC copolyester was first dissolved in *o*-chlorophenol at 80 °C to form a clear solution at a concentration of 2 wt %. These solutions contained a trace amount of insoluble particles, which were probably composed of highly crystallizable copolymers with much higher HBA contents than the average. The insoluble particles were carefully removed by filtration with 0.5 μm of pore size before casting. Two or three drops of the filtered solution were placed on a microscope cover glass, which was then put into a vacuum oven to evaporate the solvent as quickly as possible under reduced pressure at 60 °C. Most of the solvent seemed to evaporate within a few minutes, and the polymer was solidified to form a clear film on the glass surface. The film specimen on the cover glass was further dried under vacuum for 3 h at 60 °C to remove the remaining solvent completely. The films had diameter of ca. 10 mm and uniform thickness of ca. 10 μm in their center. They appeared transparent, optically isotropic, and homogeneous within the spatial resolution of a polarized light microscope (PLM). This state was kinetically frozen in the thin as-cast film specimen due to a rapid evaporation of the solvent under vacuum.

Patterns appeared in the thin films after a rapid heating to preset temperatures (*T*-jump) were investigated under PLM (Nikon Optophot-Pol XTP-11) equipped with a heating stage (Linkam Scientific Co. TH-600). Under our experimental condition, the sample temperature can reach the preset temperature of the heating stage in a period shorter than ca. 3 s. We monitored the evolution of phase-separation process in situ by CCD camera or with a roll-film. Some of heat-treated specimens were quenched from the testing temperature to room temperature in order to freeze their structures and investigate further by means of image analysis with PLM.

PLM images were taken under crossed polarizers with or without a red retardation plate (530 nm) for the films quenched after the heat treatments or in situ heat-treated at characteristic temperatures for certain periods of time. The orientations of the polarizer (P), analyzer (A), and a red plate (R) will be indicated in each figure. Because the red plate was inserted between crossed polarizers, optically isotropic domains appeared red color and anisotropic domains exhibited different colors depending on retardation of the thin film; for example bluish color shows enhanced retardation and yellowish color a suppressed retardation. Rodlike LC molecules usually possess a larger refractive index along their molecular axis than that to the perpendicular direction; therefore the spatial distribution of retardation colors in the PLM images should reflect local molecular orientation in the sample.

III. Results

III-1. N Single Phase and N/N Biphase. Figure 1 summarizes the textures elucidated in this work for the

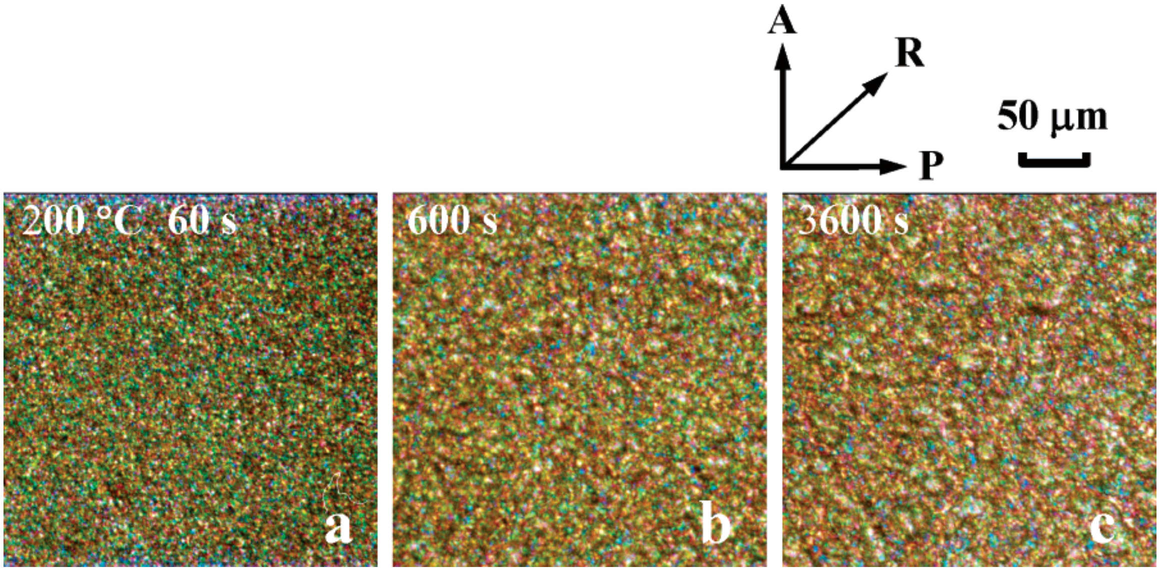

Figure 2. PLM images showing time evolution of nematic textures during isothermal heat-treatments at 200 °C for (a) 60, (b) 600, and (c) 3600 s.

LC copolyester as a function of temperature T. In our previous work[9] we assigned the T dependence as follows: the semicrystalline phase (denoted as crystallites within mesophase matrix) at $T \leq 214$ °C, N/I biphase at 215 °C $\leq T \leq 350$ °C, and I single phase at $T > 350$ °C. In this work, a special care was focused on investigation of the texture below 215 °C with isothermal annealings for a prolonged time, e.g., 2 h. As a consequence we newly found a N single phase at 190 °C $\leq T \leq 210$ °C and a N/N biphase at 210 °C $\leq T \leq 215$ °C for the same copolyester; the semicrystalline phase was pushed down below 190 °C as summarized in Figure 1.

Figure 2 demonstrates time evolution of N single phase at 210 °C. The texture is clearly shown to slowly grow as demonstrated in patterns a−c. However the growth of the pattern was almost frozen after 3600 s (pattern c). The sizes of anisotropic textures are smaller than the film thickness (10 μm) so that they overlapped along the thickness direction; hence they cannot be clearly resolved. To explore the origin of pinning of the pattern growth we investigated the thermal characteristics of the LC copolyester with differential scanning calorimetry (DSC) with scanning rate of 10 °C/min on the same as-cast film and found a small and broad endothermic peak having enthalpy of 1.0 J/g, starting from 199 °C with the tail of the higher temperature side of the peak at about 210 °C, as melting of crystallites. Although the starting film specimens used in the experiments were frozen in the amorphous state, crystallization occurred during the heating process at 10 °C/min. The corresponding exothermic peak was not observed, which is probably due to the crystallization occurred over a wide range of temperature under this condition and also to a small amount of enthalpy of crystallization. These features also reflect the composition heterogeneities of this LC copolyester. The isothermal heat-treatment at 200 °C also involves both anisotropization (i.e., transformation from vitrified isotropic state to nematic liquid crystal state) and crystallization. The crystallites formed may suppress translational diffusion of molecules in the system which slowed the growth of the nematic liquid crystal texture. In this case, the characteristic structural sizes will be kinetically determined under a balance between the growth rate of nematic structure and the crystallization rate. In a range of temperature from 190 to 210 °C near the observed highest melting point, the optically anisotropic pattern inherent in the nematic LC phase appeared, but the growth of the pattern was eventually pinned down due to the crystallization effects.

From 215 to 350 °C, the LC copolyester decomposed into the N/I biphase. The mechanism and kinetics of the N/I phase separation was fully discussed in the previous paper.[9] We only note here that the area fraction of the anisotropic phase at the long time limit and hence close to thermal equilibrium had a tendency to decrease with increasing temperature, which will be discussed later in conjunction with Figure 6.

In the isothermal annealing above 350 °C, the area fraction of anisotropic phase became smaller with time and disappeared after several minutes, and the system becomes a homogeneous isotropic phase. A temporary biphasic pattern was formed within a few seconds after the T−jump, but after 20 s, only a trace amount of anisotropic phase remained in an isotropic matrix. This point is important for the discussion in section III-3.

Our experiments in this work, which involve prolonged isothermal annealings at various temperatures with a fine temperature increment, revealed existence of the N/N biphasic region at the narrow temperature range from 210 to 215 °C as typically demonstrated by a series of patterns in Figure 3, parts a_1 to a_3, taken at 210 °C and Figure 3, parts b_1 to b_3, at 215 °C. The optical texture formed at 60 s at 210 °C (pattern a_1) was very fine and could not be well resolved due to the overlap effects of the texture along the thickness direction, as discussed earlier. With an extra annealing time, this fine structure grew. The optically anisotropic fine structures were decomposed into N/N biphase structure in which nematic domains having a higher order parameter and a lower order parameter coexisted (patterns a_2 and a_3 in Figure 3). The N phase having a lower order parameter at 215 °C was observed to be transformed into isotropic phase upon slightly elevating temperature above 215 °C, while other phase was still kept anisotropic. Thus, we observed N/I biphase structure at higher temperatures. We will discuss the mechanism of N/N biphasic pattern formation in detail later (section IV-1).

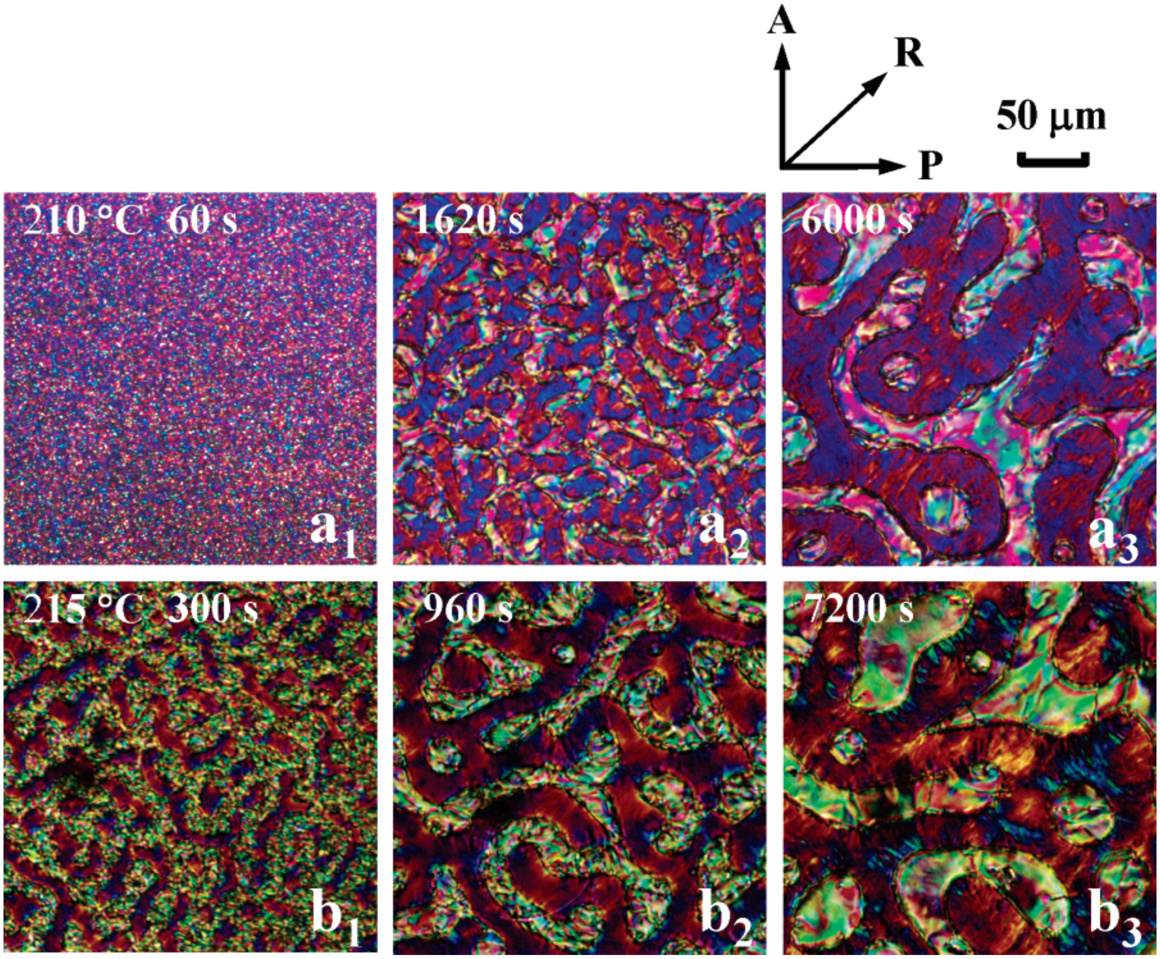

Figure 3. Series of the N/N biphase patterns formed during isothermal heat-treatments at 210 and 215 °C: (a_1) 60, (a_2) 1620, and (a_3) 6000 s at 210 °C; (b_1) 300, (b_2) 960, and (b_3) 7200 s at 215 °C.

III-2. Memory Effect on Cooling Process. PLM images in Figure 4 were taken in the same area of the same specimen on a cooling process with 10 °C/min after isothermal heat treatment at 300 °C for 60 s in the N/I biphase region. Pattern a was taken before the cooling process but after the isothermal annealing at 300 °C for 60 s, while patterns b−d were taken at 249, 240, and 210 °C during the cooling process, respectively. Part e schematically illustrates the thermal protocol. In each pattern the red part is isotropic phase, while another part is anisotropic. The coarsening of the N/I phase-separated domains continued until temperature was cooled to 249 °C (pattern b). On the further cooling process down to 240 °C (pattern c), the pattern appeared to be almost frozen due to the fact that the coarsening rate of the pattern became slower than the cooling rate. At the same time the red isotropic matrix phase partially indicated optical anisotropy, especially at a periphery of the interface of the anisotropic domains (see patterns b and c), reflecting a spatial concentration gradient of the HBA moiety such that it decreases with a distance from the interface. It must be build up during the isothermal annealing at 300 °C. Eventually at 210 °C the N/I phase-separated pattern changed to the pattern having two anisotropic phases as shown in pattern d. It should be recalled that the N/N biphase structure exists between 210 and 215 °C at thermal equilibrium as shown in Figures 1 and 3. However the phase structure of the LC copolyester turned to N/N biphasic pattern at a temperature somewhat below 215 °C, which may be reasonable for the reason as described below.

The isotropic phase at 300 °C shown in the matrix of Figure 4a is expected to contain an amount of HBA moiety which is smaller than the average amount. Because the LC copolyester used in the experiments had a broad bimodal composition heterogeneity, the system should have a distribution of nematic−isotropic transition temperature. It is expected that a fraction of LC copolyester molecules having a lower HBA moiety (hence having less rigidity) is segregated into the isotropic phase at 300 °C. Consequently the isotropic to nematic transition of the isotropic domain occurs at a lower temperature than 215 °C in the cooling process. On a cooling process, the pattern formation was influenced by thermal histories prior to the cooling through a spatial distribution of HBA composition generated by the phase separation into nematic and isotropic phases. The N/N biphasic pattern can be controlled as a memory effect of N/I biphasic pattern in this case.

III-3. Pattern Formation on Quenching Process. Figure 5 shows PLM images for the films subjected first to isothermal heat treatment at various temperatures for 60 s at (a) 300 and (b) 340 °C in the N/I biphase region and (c) 350 and (d) 390 °C in the I phase and then quenched rapidly to room temperature within a few seconds. The thermal protocols for parts a−d are schematically shown in part e. It should be noted that all the isothermal heat-treatments given in Figure 5 develops a phase separation into anisotropic domains

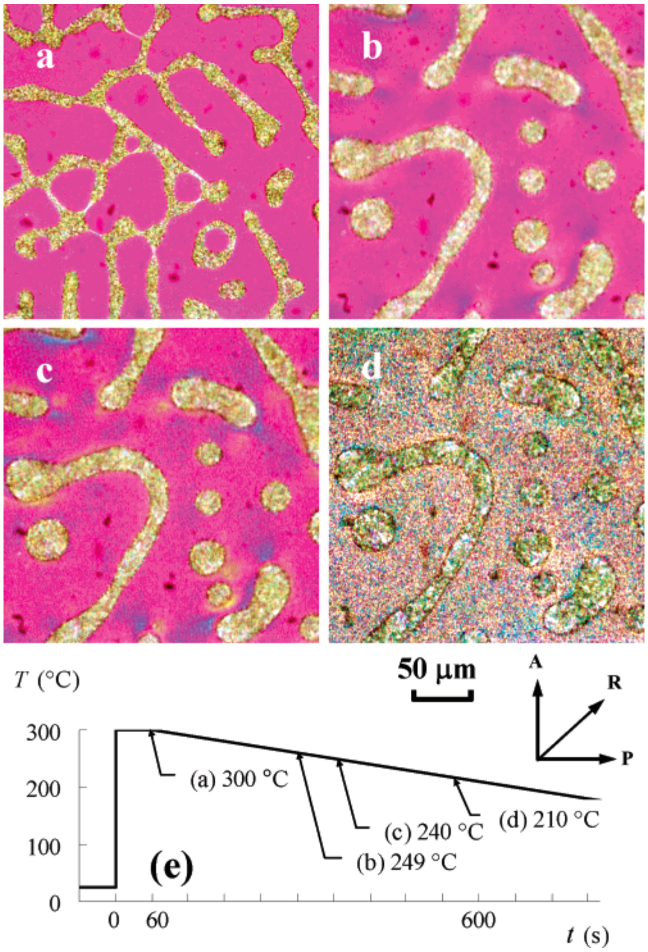

Figure 4. Series of PLM images taken in the same area of the specimen. The specimen was first annealed at 300 °C for 60 s in the N/I biphasic region (see Figure 1), followed by cooling with 10 °C/min.; (a) specimen isothermally annealed at 300 °C for 60 s before cooling and specimens (b) at 249, (c) 240, and (d) at 210 °C on the cooling process. Note that the system becomes N/N biphase at 210 °C. Part e schematically shows the thermal protocol.

in the matrix of isotropic phase. Four images in Figure 5 were taken under the cross polarizers without a red retardation plate. Therefore, an isotropic phase appeared dark. The anisotropic domains which existed at the end of the heat treatment at each temperature appeared yellow and the rest of the area was isotropic. The higher the temperature, the smaller is the amount of copolyester which remains in the anisotropic phase and hence the smaller is the yellow area of the anisotropic domains. A comparison of the PLM images in Figure 5 with those obtained in situ at the end of the heat treatment at each temperature (not shown in this paper) elucidated the fact that a part of the isotropic areas in Figure 5 was transformed into anisotropic phase during the quenching process.

In the specimen quenched from 300 °C (part a) a small anisotropic area is developed in the periphery of interface of the phase-separated domains during the quench process. Let us designate the growth of anisotropic area or volume formed during quenching as “extra anisotropization”. At higher heat treatment temperatures as shown in patterns b−d, the extra anisotropization extended to a larger area in the isotropic phase, while the area or volume of “originally” anisotropic phase, which has orange color and existed before quenching, became smaller. This extra anisotropization and resulting anisotropic domains grew always from the interface of the two coexisting phases toward the interior of the “originally” isotropic phase as shown in pattern b quenched from 340 °C. In pattern c quenched from 350 °C, most of the area of the “originally” isotropic phase turned to the anisotropic phase due to the extra anisotropization. The “originally” isotropic phase existing in situ at 390 °C turned into the fully anisotropic phase with an interesting Schlieren texture as shown in Figure 5d during the cooling process. Here the originally existed anisotropic domains appear to act as centers for the wedge disclination.

The extra anisotropization and extra anisotropic phase created during the quenching process reflects an average composition of HBA moiety in the isotropic phase before the quenching, $\langle \phi_{\mathrm{HBA}} \rangle$, and a spatial distribution of the HBA moiety, $\phi_{\mathrm{HBA}}(r)$, across the interface. Part f schematically presents a model for a spatial distribution of ϕ_{HBA} across the interface of the originally anisotropic domains as a function of the reduced distance r/d from the interface, where d is an average interdomain distance. Here ϕ_c designates a critical HBA concentration required for the anisotropization at the given quench condition. In the case of patterns a and b, ϕ_{HBA} rapidly drops with r/d below ϕ_c, so that the extra anisotropization occurs only in the periphery of the interface, while in the case of patterns c and d, ϕ_{HBA} appears to be greater than ϕ_c everywhere in the space, even at $r/d \approx 1/2$, so that the extra anisotropization extends over the whole space of the isotropic matrix.

IV. Discussion

IV-1. Nematic Single Phase and Nematic/Nematic Biphase under Thermal Equilibrium. The brighter domains in the N/N biphase in Figure 3 (patterns a_2−a_3 or patterns b_1−b_3) showed optical textures typical to nematic mesophase. The other domains with a darker contrast also exhibit optical texture inherent in nematic mesophase. The brighter nematic domains having higher order parameter than the darker nematic domains keep the optical anisotropy up to higher temperatures and should be comprised of more rigid molecules with a higher HBA content than the average. On the contrary, the domains with lower order parameter should contain more flexible molecules with a less HBA fraction. The anisotropic phase having lower order parameter changed to isotropic one above 215 °C, but the anisotropic phase having higher order parameter was conserved above 215 °C, giving rise to the transformation from N/N biphasic patterns to N/I biphasic patterns; the N/N biphase exists only in the narrow temperature range.

The N/N biphasic patterns appeared to imply that the LC copolyester system was composed of approximately two kinds of polymers having different average compositions of HBA and hence having different nematic to isotropic transition temperatures. If the two polymers have similar average compositions, the N/N biphase may exist over a wide range of temperature before one of them is transformed into isotropic phase with increasing temperature. However such systems having similar average compositions may not exhibit the N/N biphase but rather tend to stay in N single phase. On the other hand, if the two polymers have different average compositions, they tend to phase separate into

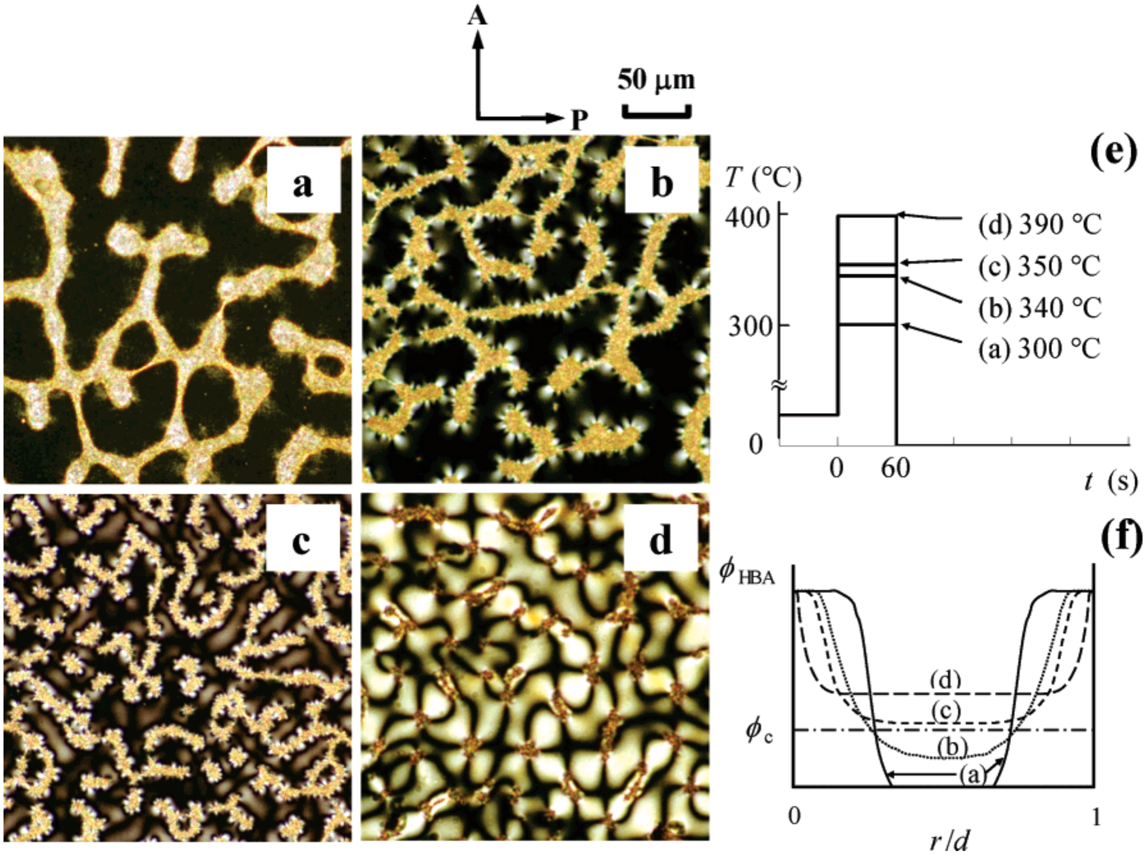

Figure 5. PLM images without retardation plate for films subjected first to isothermal heat treatment at various temperatures, (a) 300, (b) 340, (c) 350, and (d) 390 °C, for 60 s and then quenched to room temperature. Note that the system before the quench is in the N/I biphase up to 350 °C but in the I single phase at 390 °C. Parts (e) and (f) schematically present, respectively, the thermal protocol and spatial distribution of fraction of the HBA moiety (a mesogenic group), ϕ_{HBA}, as a function of the reduced distance of *r*/*d* where *d* is the interdomain distance and ϕ_c is the critical concentration of the HBA moiety required for anisotropization.

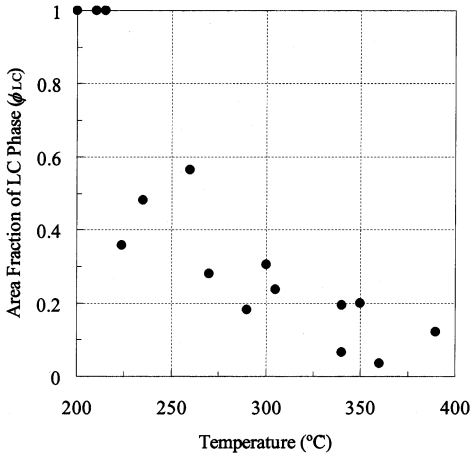

Figure 6. Temperature dependence of the area fraction of liquid crystalline phase (ϕ_{LC}) in phase-separated patterns obtained after isothermal heat treatment at various temperatures for 60 s.

the N/N biphase. However the phase having a lower HBA content is soon transformed into isotropic phase, while other phase stays anisotropic phase up to high temperatures, so that N/N biphase appears only in a narrow temperature range. Thus, we expect that the temperature range for the N/N biphase depends on composition heterogeneity of HBA and on a subtle balance between the phase separation due to composition heterogeneity and the thermodynamic stability of the nematic phase having a lower average HBA content.

Comparisons of the patterns a_3 and b_3 in Figure 3 with those observed for the N/I biphase patterns having comparable sizes and comparable volume fraction of the two phases revealed that area-averaged Gaussian and mean curvatures are smaller in the N/N phase-separated domains than in the N/I phase-separated domains. This may be because the free energy cost of the elastic (bending) deformation for the growth of phase structure is larger in the former than in the later.

We would like to add some remarks on the observed trend of transformation from N single phase to N/N biphase. It is not surprising at all to find N/N biphase for binary N/N polymer blends. However for the binary N/N blends it would be difficult for us to explain the low-temperature N single phase from the viewpoint of a conventional phase diagram. One would expect N/N, crystal/N and crystal/crystal two phase coexistence at lower temperatures, because the two phases have their own crystal−nematic transitions. One may treat the N/N biphase in the neat LC copolyester as a consequence of a hypothetical N/N blend having different fraction of HBA moiety. In this case one should note an important difference between the hypothetical N/N blend and the conventional N/N blend. In the neat LC copolyester in the N/N biphasic temperature region, the "blend" composition may not be constant with temperature as in the case of the binary N/N blends. A composition (defined as ϕ_L) of the component which forms N phase having a lower order parameter (defined as L) depends on temperature. As temperature is lowered, a fraction of molecules in L having relatively higher HBA content may increase their rigidity and hence may be incorporated into the N phase having a higher order parameter, giving rise to a degrease of ϕ_L with decreasing T. At a sufficiently low temperature ($T \leq 210$ °C), ϕ_L goes to zero and hence single N phase may be attained. This is a kind of induced nematic ordering upon lowering temperature. This induced ordering may occur more easily for the neat LC copolyester having an appropriate composition distribution than for the conventional binary N/N polymer blends. The temperature dependence of the "blend composition" in the neat LC copolyester as the hypothetical blend is much more obvious in the N/I biphase temperature region as will be discussed in the next section (IV-2).

Finally, we should point out that we cannot completely rule out a possibility of N single phase is a consequence of trapped nonequilibrium phase because of the slowing down of the growth of nematic texture due to crystallization effect at $T \leq 210$ °C as discussed earlier. If the texture grew to a sufficiently larger size, N single phase might eventually phase-separate into N/N biphase.

IV-2. Temperature Dependence of Area Fraction for Anisotropic Phase in the N/I Biphase Region. A number of the N/I phase-separated patterns was taken after the isothermal heat-treatment process at various temperatures but for the same period of time of 60 s. They were binarized into bright and dark areas with an image analyzer, where bright and dark areas correspond to anisotropic and isotropic phases, respectively. Area fraction of liquid crystalline phase (ϕ_{LC}) was evaluated and plotted as a function of the heat-treatment temperature in Figure 6. The patterns appeared below 215 °C were either the single anisotropic phase or the N/N biphase, thus ϕ_{LC} always stayed at 1.0, independent of temperature. Above 215 °C, however, the anisotropic phase having a lower order parameter transformed to the isotropic phase, resulting in the N/I phase-separated patterns. As a consequence, ϕ_{LC} dropped suddenly down to approximately 0.5. Thus, the volume fractions for the coexisting nematic phases immediately below 215 °C are expected to be equal. Then ϕ_{LC} approached monotonically to zero, i.e., fully isotropic phase, with increasing temperature from 215 to 390 °C.

The composition heterogeneity of the LC copolyester was identified as a bimodal elution profile on HPLC as shown in Figure 13 of ref 9. Further NMR analysis indicated that the molar ratio of HBA and ET units for the eluted part rich in the HBA unit (designated as Fr. 1) was 58/42 and that for the eluted part poor in the HBA unit (designated as Fr. 2) was 47/53. The weight fractions of Fr. 1 and Fr. 2 are 0.25 and 0.75, respectively. The bimodal distribution on the molecular composition is considered to originate from the difference in the reactivity between monomers on the polymerization process as is well-known for these kinds of copolyester.[4,5,12] In a sense this neat LC copolyester is approximated to be a polymeric mixture composed of two different chemical fractions, although it is fundamentally different from a binary mixture of nematic/isotropic or nematic/nematic polymer blends for the reason as already clarified in section IV-1 for the transformation between N single phase and N/N biphase and also for the reason as will be described in the next paragraph for N/I biphase. Molecules in Fr. 1 contain more HBA residues to give higher chain rigidity than in Fr. 2; therefore, Fr. 1 should give favorable effects on forming LC phases up to higher temperatures. It is also important to note that the composition difference between the two fractions is rather small.

Despite the clear bimodal composition distribution, the volume of the two phases did not keep a constant value when temperature was changed, but rather the volume of the anisotropic phase decreased continuously with raising temperature above 220 °C as shown in Figure 6. To interpret the temperature dependence of ϕ_{LC}, we should take into account effects of the temperature dependence of the critical composition of HBA required for the polymer molecules to be kept in the anisotropic phase. As the temperature increased, a larger fraction of polymer molecules could not be incorporated into the nematic phase because the molecules are required to have a higher concentration of HBA units in order for them to be kept in the anisotropic phase. The polymer molecules having a lower HBA content may be segregated out from the anisotropic phase to isotropic phase, resulting in thinning of anisotropic domains with increasing temperature. In this sense the neat LC copolyester is fundamentally different from a binary mixture of nematic/isotropic polymer blends, and cannot be treated as a hypothetical blend of Fr. 1 and Fr. 2 with the fixed blend composition (25 wt %/75 wt %), simply because the "composition" of the "blend" depends on temperature. On the basis of the same reason, the neat LC copolyester is different from a binary mixture of nematic/nematic blends.

The information on $\phi_{LC}(T)$ obtained in this section is also important for the discussion in the next section (IV-3).

IV-3. Seeded Growth of LC Domains. Here we consider self-assembling of the LC copolyester under the following particular nonequilibrium path way. The optically isotropic and homogeneous as-cast films are first subjected to T−jump to $T_x = 380$ or 390 °C above 350 °C where the system attains fully isotropic phase at thermal equilibrium, as shown in Figure 1. The system is annealed at T_x for a certain time t_x and then subjected to quenching to room temperature for investigation of the vitrified self-assembling structures, developed under this particular thermal history as schematically illustrated in Figure 7c. Some typical results on the structures are demonstrated in Figures 7 and 8. We shall describe below the backgrounds of the anticipated self-assembling processes.

During the course of the T−jump process and the annealing process, the system is anticipated to pass through a series of stages involving formation of the N phase, the N/N biphase, the N/I biphase, and eventually the I phase, depending on the time spent t_x at T_x. Under the condition given by (t_x, T_x) in Figures 7 and 8, the system attained the N/I biphase structure: The yellow domains or red-brown domains in Figure 7, parts a and b, which are locally percolated, and the red-brown domains in Figure 8, which are more isolated and more spherical compared to those in Figure 7, reflect the anisotropic domains coexisted with the isotropic matrix, defined hereafter "preexisting" anisotropic domains at (t_x, T_x) before quenching to room temperature.

During the quenching, the system again should pass through, in principle and in a general sense, the series of stages of N/I, N/N, N phase, and eventually solidified by crystallization and vitrification, resulting in the observed structures shown in Figures 7 and 8. However the initial stage of the system before quenching was the

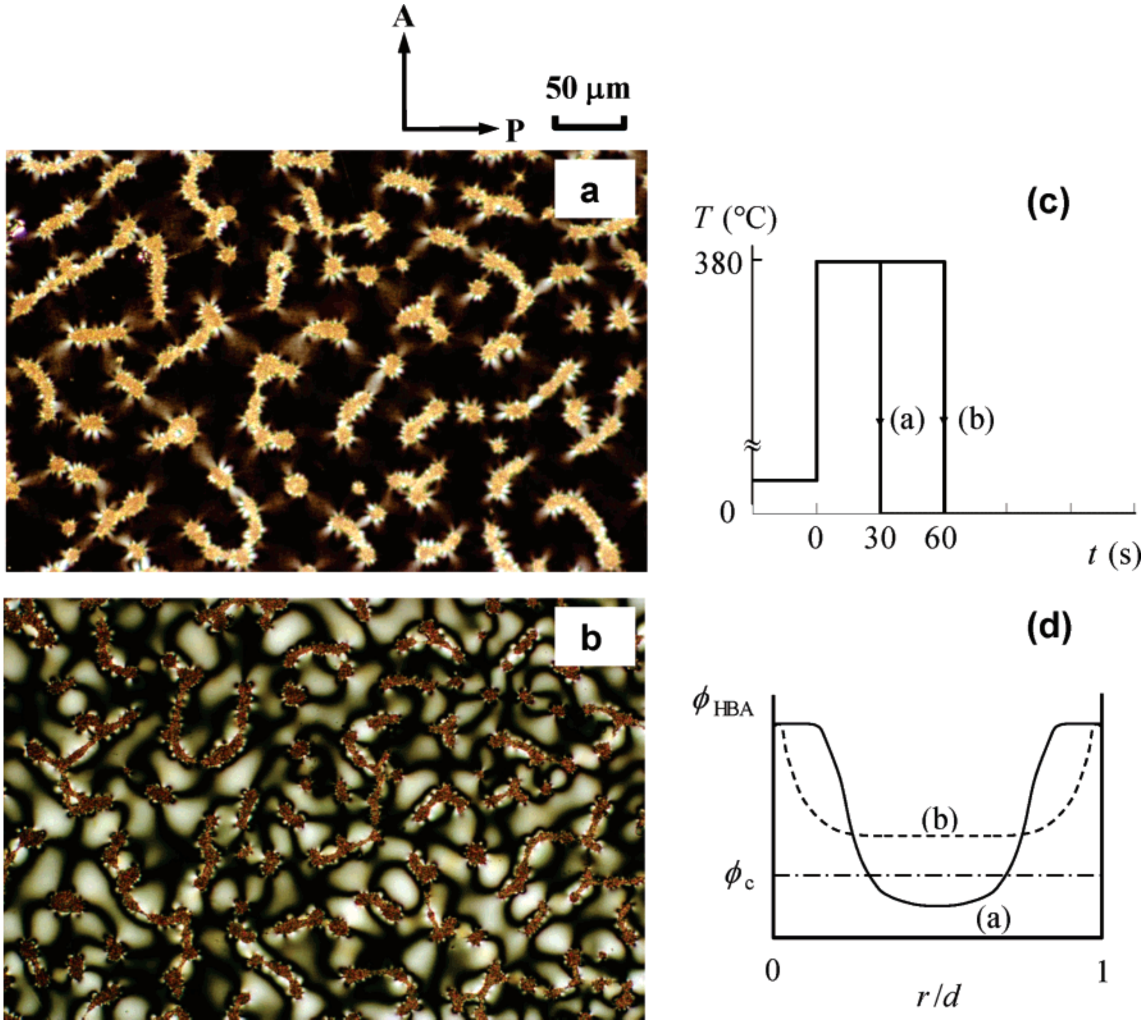

Figure 7. PLM images without retardation plate for the thin films subjected first to isothermal heat treatment at 380 °C for (a) 30 and (b) 60 s in the I single phase and then quenched to room temperature. Parts c and d schematically present, respectively, the thermal protocol and spatial distributions of the HBA moiety.

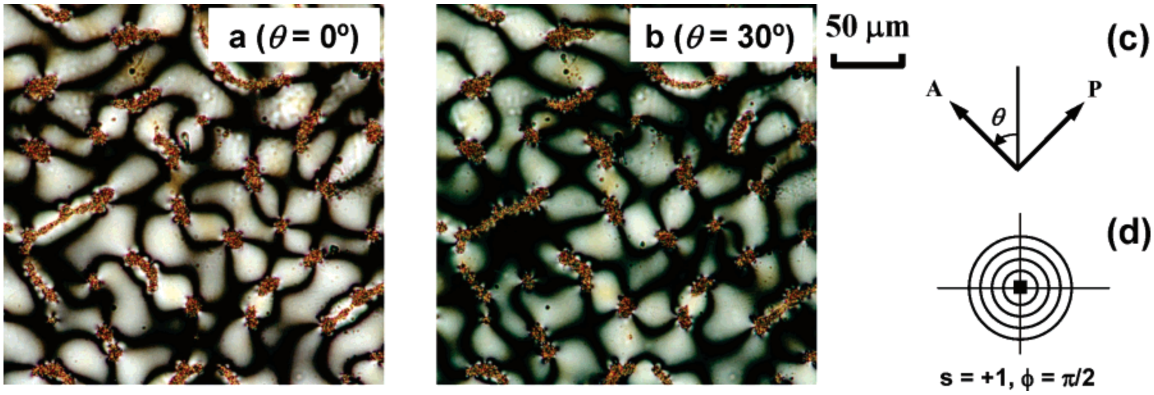

Figure 8. PLM images without retardation plate taken in the same film subjected first to isothermal heat treatment at 390 °C for 60 s in the I single phase and then quenched to room temperature. (a) and (b) Micrographs between crossed polarizers with a different angle θ as defined in part c; (a) $\theta = 0°$ and (b) $\theta = 30°$. Note that preexisting anisotropic domains which are left in the annealing process act as seeds to give wedge disclination of strength $s = +1$ and $\phi = \pi/2$ (part d) in the matrix phase during the quenching process.

biphase, and consequently, each phase has an average composition of HBA and composition distribution of HBA different from those in the as-cast films. Consequently the stages experienced by each phase during the quenching process should be different from those during the T−jump and annealing process of the as-cast film. During the rapid quenching process involved in this experiment, the preexisting anisotropic domains or phase is expected to be essentially unaltered and simply vitrified. The isotropic phase or matrix coexisted with the preexisting anisotropic domains may not have such a broad composition distribution of HBA as that in the as-cast films so that it would not involve N/I phase separation during the quenching but rather involve only ordering into nematic domains in the regions having a high HBA content in the matrix phase.

Now we shall focus below on this ordering process of the isotropic matrix, containing the preexisting anisotropic domains as seeds, into nematic domains during the quenching process. We believe the following three important factors are underlying in this process. (i) The volume fraction $\phi_{LC}(t_x, T_x)$ of the preexisting anisotropic domains decreases as a function of increasing T_x and prolonged t_x. As a consequence the locally percolated anisotropic domains in Figure 7 become thin and tends to be disrupted with increasing t_x from 30 s (part a) to 60 s (part b). The same trend was observed with increasing T_x from T_x = 380 °C (Figure 7b) to 390 °C (Figure 8) at a given t_x of 60 s. The locally percolated domains in Figure 7b is degenerated to essentially isolated and, more or less, round droplets in Figure 8. This process involves (ii) diffusion of molecular species having a smaller HBA content from the anisotropic domains into the matrix across the interface, resulting in (ii-a) increasing average content of HBA in the isotropic matrix and (ii-b) building up a transient concentration gradient of HBA units across the interface $\nabla\ \phi(t_x, T_x)$. When the system is quenched after the annealing at T_x for t_x, temperature is lowered below the isotropic-to-nematic transition temperature of the matrix phase, so that (iii) the ordering into nematic domains may occur in the isotropic matrix, depending on the local concentration of the HBA moiety. The system is eventually solidified via crystallization and vitrification.

From the above arguments, it may be elucidated that the self-assembling structures developed under this particular nonequilibrium path way are strongly affected by a spatial distribution of HBA units across the interface of the preexisting anisotropic domains, which is, in turn, affected by the diffusion rate and the rate of nematic ordering in the isotropic matrix. Thus, the ordered structures should reflect and reveal fundamental physics concerning $\nabla\phi(t_x, T_x)$, or the competition between the diffusion rate, and the ordering rate.

In the case of Figure 7a, t_x is not long enough so that the tail of $\nabla\phi(t_x; T_x)$ would not extend far from the interface and that the middle part of the isotropic matrix, surrounded by the preexisting anisotropic domains, would still have a small HBA content as schematically shown by curve *a* in Figure 7d. Thus, the ordering into nematic domains occur only in the periphery of the preexisting domains, giving rise to unique dendritic anisotropic domains in the matrix of the isotropic phase. The prolonged t_x (60 s) as in the case of the result shown in Figure 7b would give rise to an overlap of the tail of $\nabla\phi(t_x, T_x)$ from the neighboring preexisting domains as schematically shown by curve *b* in Figure 7d, so that most of the area in the isotropic matrix is transformed into nematic phase during the course of the quenching. The dark region is the region where the directors are nearly parallel to the electric vector of either polarizer or analyzer, because the dark regions are turned into bright when the cross polarizers are rotated. In the periphery of the preexisting anisotropic domains we can observe the same dendritic features having higher optical anisotropy than the rest of the matrix, and in the matrix we can observe the Schlieren texture with dark brushes, as seen in Figure 7b.

The prolonged t_x (60 s) at higher T_x (390 °C) as in the case of the result demonstrated in Figure 8 decreases the volume fraction of the preexisting anisotropic domains due to cooperative diffusion of polymer species having a relatively lower HBA fraction into isotropic matrix across the interface. Thus, the preexisting anisotropic domains are isolated and tend to become more or less spherical. They are located with a roughly equal distance in space, as they originated from spinodally decomposed domains of the N and I phases.[9] We can observe four dark brushes oriented nearly parallel to the polarizer or analyzer axis which are emanating from the preexisting nearly spherical anisotropic domains as demonstrated in Figure 8. The brushes were observed to be rotated in the same direction as the rotational direction of the cross polarizers (θ in part c) as shown in parts a and b. Thus, these preexisting anisotropic domains seem to serve as seeds for the formation of the LC phase with the wedge disclination of strength $s = +1$ and $\phi = 0$ or $\pi/2$, being either tangentially or radially oriented directors around the seeds, respectively. Close observation of retardation color induced by red retardation plate revealed evidence that directors are aligned tangentially on average, as schematically shown in part d.

We should note that neat nematic phase has wedge disclinations of the strength $s = \pm 1/2$ as thermodynamically most stable defects. This implies that the surfaces of preexisting domains control orientation of directors, creating thermodynamically less stable disclination. In the very periphery of the anisotropic domains, we can observe the strong anisotropic (dendritic) pattern similar to that found in Figure 7. This may reveal that (i) the preexisting anisotropic domains serving as seeds have interface roughness, seemingly originated from viscous fingering,[13] and (ii) local orientation of directors very close to the interface follows surface roughness of the seeds, giving rise to local variation in the director orientation along the interface, which may be an origin of the dendritic feature developed from the seeds. The interface-roughness-induced local variation of directors will be damped away with increasing the radial distance from the interface, giving rise to the average tangential orientation of directors as modeled in Figure 8d.

V. Conclusion

The pattern formation via phase separation in a thin film of a *neat* main chain type liquid crystalline (LC) copolyester has been investigated in a wide range of temperature. As-cast films of the LC copolyester having optically homogeneous and isotropic property, as a trapped nonequilibrium structure and property, were first prepared by the solvent casting method as described earlier. The ordering process of the as-cast copolyester films induced by the isothermal annealing was observed in situ at various temperatures under polarized optical microscopy. Upon increasing temperature, the system exhibited nematic (N) single phase, N/N biphase, N/I biphase, and optically isotropic (I) single phase. N/N biphase appeared in a narrow temperature range limited by the low N−I transition temperature of the anisotropic phase having a lower HBA content. The observed patterns are believed to be a consequence of phase separation driven by composition heterogeneities of the LC copolyester. Especially a change of the pattern from N single phase to N/N biphase with increasing temperature, which are newly found in this work, are proposed to be unique to the neat LC copolyester having the bimodal composition distribution. We pointed out this trend is difficult to be explained in terms of the phase behavior of a conventional binary mixture of N/N polymer blends in section IV-1.

Interesting nonequilibrium textures were observed by first applying isothermal annealing of the specimen at the temperature over ca. 215 °C in the N/I phase or over ca. 350 °C in the single I phase for varying time, followed by quenching of it to room temperature. These are "dendritic anisotropic LC texture" as demonstrated in Figures 5b, 5c, and 7a and impurities-induced Schlieren texture with disclination lines having strength $s = +1$, as discussed in detail in section IV-3 in conjunction with Figure 8. This annealing and quenching process involves first the formation of phase separation into anisotropic domains in the isotropic matrix in the annealing process, followed by formation of nematic LC domains within the isotropic matrix during the quenching process. The isotropic matrix, which undergoes isotropic-to-nematic transition during the quenching process, coexists with preexisting anisotropic domains. These anisotropic domains act as seeds for the nematic ordering in the isotropic matrix during the quenching process.

The dendritic anisotropic LC texture formed in the periphery of preexisting anisotropic domains is a consequence of a transient concentration gradient of molecular species having a high HBA content formed in the periphery of the preexisting anisotropic domains which is built up in the first annealing process. The local HBA content is expected to decrease with a distance from the interface of the preexisting anisotropic domains, and this concentration gradient is responsible for the epitaxial growth of LC phase from the interface of the preexisting anisotropic domains toward the isotropic matrix during the quenching process. The dendritic feature seemingly reveals that the preexisting domains have interface roughness, probably originated from viscous fingering in the isothermal annealing process, and the directors of the ordered phase near the interface follow the interface roughness. The observed phenomenon, which belongs to the class of nonequilibrium solidification phenomena, deserves future experimental and theoretical works.

The Schlieren texture with disclination lines having strength $s = +1$ and $\phi = \pi/2$ reveals also the epitaxial growth of LC phase in a sense that the interface of preexisting anisotropic domains, which are isolated and almost round in shape in the isotropic matrix, act as seeds for wedge disclination centers and controls energetically unfavorable orientation of directors of nematic liquids when isotropic-to-nematic phase transition occurs in the isotropic matrix during the quenching process. This is considered to be impurity- (or seed-) induced nonequilibrium wedge disclination.

Acknowledgment. We are grateful to Dr. Kishiro and Mr. Sakata, Mitsubishi Chemical Co., for kindly suggesting the composition analysis of the copolyester. We thank Polyplastics Co., Ltd. for partial financial support of this work.

References and Notes

(1) Blackwell, J.; Cheng, H.-M.; Biswas, A. *Macromolecules* **1988**, *21*, 39.
(2) Nicely, V. A.; Dougherty, J. T.; Renfro, L. W. *Macromolecules* **1987**, *20*, 573.
(3) Laus, M.; Angeloni, A. S.; Galli, A.; Chiellini, E. *Macromolecules* **1992**, *25*, 5901.
(4) Mathew, J.; Ghadage, R. S.; Ponrathnam, S.; Prasad, S. D. *Macromolecules* **1994**, *27*, 4021.
(5) Jackson, W. J.; Kuhfuss, H. F. J. *Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2043.
(6) Zachariades, A. E.; Economy, E. J.; Logan, J. A. *J. Appl. Polym. Sci.* **1982**, *27*, 2009.
(7) Zachariades, A. E.; Logan, J. A. *Polym. Eng. Sci.* **1983**, *23*, 797.
(8) Joseph, E.; Wilks, G. L.; Baird, D. G. *Polymer* **1985**, *26*, 689.
(9)) Wang, W.; Shiwaku, T.; Hashimoto, T. *Macromolecules* **2003**, *36*, 8088.
(10) Nakai, A.; Shiwaku, T.; Wang, W.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1996**, *29*, 5990.
(11) Nakai, A.; Shiwaku, T.; Wang, W.; Hasegawa, H.; Hashimoto, T. *Polymer* **1996**, *37*, 2259.
(12) Mathew, J.; Ghadage, R. S.; Lodha, A.; Ponrathnam, S.; Prasad, S. D. *Macromolecules* **1997**, *30*, 1601.
(13) Toth-Katone, T.; Borzsonyi, T.; Buka, A. *Mol. Cryst. Liq. Cryst.* **2000**, *339*, 175.

MA050042D