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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · APRIL 2006

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Surface Microcracks Decoration and Disclination Defects of Wholly Aromatic Liquid Crystalline Copolyesters

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Received: September 28, 2005; In Final Form: January 15, 2006

An intensive study has been conducted to map the director fields of disclination of nematic liquid crystalline copolyesters. In this study, films of two wholly aromatic main-chain polyesters containing para- (ABA/MH/TFTA) and meta-linkages (ABA/MH/TFIA) (ABA, *p*-acetoxybenzoic acid; MH, maleic hydrazine; TFTA, tetrafluoroterephthalic acid; TFIA, tetrafluoroisophthalic acid) were synthesized to investigate the effects of kinks on liquid crystallinity, disclination strength (S), and surface microcracks decoration. These two copolyesters were prepared by *in-situ* thin film polymerization and characterized by polarizing light microscope, wide-angle X-ray diffraction, as well as “rotational isomeric states” (RIS) Metropolis Monte Carlo (RMMC) simulation. An optical microscope shows that the surface microcracks forms in the nematic–mosaic texture during a rapid quenching. The ABA/MH/TFTA film exhibits disclination strength with $S = +1$ and $S = -1/2$; however, disclination strengths with $S = \pm 1$ have been observed in the ABA/MH/TFIA system. To our best knowledge, this is the first paper reporting the effects and evidence of kink (meta and para moieties) on topological defect of disclination. In addition, the RMMC analysis supports the liquid crystal formation in both polyester films with a persistence ratio greater than 6.42.

1. Introduction

Main-chain liquid crystalline polymers (MCLCPs) have been used as high performance materials because of their sophisticated properties, such as good mechanical properties, good dielectric characteristic, and excellent thermal stability.^{1–4} Studies of the disclination in liquid crystalline polymers (LCPs) have received great interest because of their important effect on rheological behavior and alignment properties. The disclination defect is a commonly observed phenomenon in liquid crystals (LCs) and represents the discontinuity in the director field of mesogen director orientation in space. The observation of director fields around disclination is one of the easiest techniques to investigate the molecules' director orientation and understand the possible defects in a given ordered medium.

To date, four experimental methods have been developed to investigate the molecular director around disclination of LCPs: surface microcracks decoration,^{5–9} band-texture decoration,^{10–12} lamellar decoration,^{13–17} and focal–conic texture decoration.^{18,19} The surface microcrack, band-texture decoration, and lamellar decorations were reviewed by Qian et al.²⁰ in 1995, while focal–conic texture decoration was discovered only in 2000.

Generally, the surface microcracks decoration appears when there is solidification of molten liquid crystal in thermotropic LCPs^{5–8} or after evaporation of solvent in a lyotropic LCPs.⁹ For thermotropic LCPs, the molecules of highly rigid chains that are well oriented tend to form aligned chain bundles and/or fibrils in LCPs domains when the molten nematic LC is frozen rapidly. During the solidification of LC melt, cracks easily emerge along the fibrils and/or chain directions because

of the weak lateral interchain cohesion in the nematic melt.⁷ Typically, the mapping of director fields by the surface microcracks decoration can be obtained in both MCLCPs and side-chain liquid crystalline polymers (SCLCPs). In MCLCPs, it is speculated that the microcracks are along the direction of the chain. Hence, the director orientation that is coherent to the direction of polymers' backbone gives a definite image of the director fields around disclination. On the other hand, in SCLCPs, the relationship between the director fields of the mesogen units in the side chain and polymers' backbone is uncertain. Yet, the published literature on director fields of disclination is still limited to MCLCPs and/or high rigidity SCLCPs. Basically, this decoration method is applicable to thin films, which have about 50 μm thickness, and the microcracks study is conducted using an optical microscope with or without a polarizer.

Several studies involving the formation of surface microcracks by solidification of nematic melt have been reported.^{5–8} Wittler et al.⁵ found surface cracks on a solution-cast poly(2,5-didodecyl-1,4-phenylene) when it was cooled from its melt, and annealed at 150 °C as well as 135 °C followed by a rapid quenching. For these cracks, disclination of strength $S = \pm 1/2$, ± 1 , and $\pm 3/2$ were discovered. Subsequently, two semiflexible copolyesters were studied by Hudson et al.⁶ A schelieren texture with disclination $S = \pm 1$ was observed in these thin films using an optical microscope, while the surface was found to be microcracked with disclination $S = \pm 1/2$ using a transmission electron microscope (TEM). Hu et al.⁷ reported the observation of the director fields around disclination by solidification-induced band texture and surface microcracks decoration. They found that the preshearing was a crucial step for formation of microcracks. A few disclination field patterns, such as $S = \pm 1/2$ and ± 1 , were observed and connected by the inversion wall in the direction of preshearing. Recently, our group has conducted

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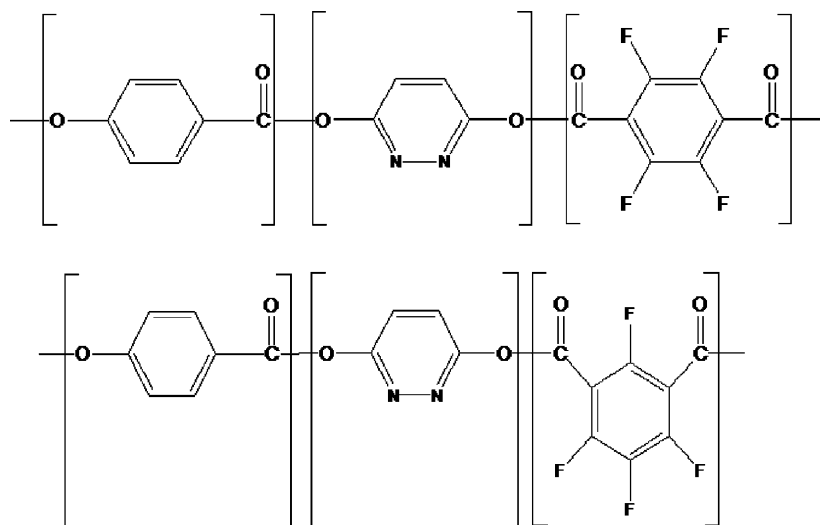


Figure 1. Chemical structures for (a) ABA/MH/TFTA (para-linkage) and (b) ABA/MH/TFIA (meta-linkage) systems.

an *in-situ* thin film polymerization of thermotropic liquid crystalline copolyesters and characterized their phase behavior.⁸ Surprisingly, surface microcracks with $S = +1$ disclination and striped microcracks were observed with the solidification of molten nematic–mosaic texture at room temperature.

On the other hand, a study involving the formation of surface microcracks during evaporation of solvent was reported by Wang et al.⁹ A film of polydiacetylene with urethane as side group was cast from chloroform and displayed a typical schlieren texture. After the solvent evaporation, surface microcracks appeared while the schlieren texture remained. These cracks revealed the director fields of disclination strength with $S = \pm 1/2$ and ± 1 . From the above approaches, it is clearly shown that the studies focused on the director fields of strength in the disclination core. In addition, although much research has been conducted to investigate and understand the disclination core-structure relationship of LCs and LCPs, a thorough understanding of the factors that determine the creation of topological strength of the disclination is still limited. Furthermore, to our best knowledge, (1) the observation of a striped pattern of anisotropic microcracks in the domains (nematic–mosaic) texture and (2) the influences of kink linkage on topological defect of disclination have not yet been reported.

The aim of this study is to extend our previous study on MCLCPs which have the pyridazine heteroatom and investigate the topological defects of disclination. In this paper, we attempt to examine in detail the surface microcracks decoration of para- (ABA/MH/TFTA) and meta-linked (ABA/MH/TFIA) copolyesters using a polarizing light microscope (PLM). In addition, the effect of reaction temperature and monomer composition on LCs and surface microcrack formation will also be investigated. A computational simulation (“RIS”) Metropolis Monte Carlo simulation is employed to study the LCPs’ chain properties.

2. Experimental Section

2.1. Materials. The monomers used in this study were *p*-acetoxybenzoic acid (ABA), maleic hydrazine (MH), tetrafluoroisophthalic acid (TFIA), and tetrafluoroterephthalic acid (TFTA). ABA was synthesized by acetylating *p*-hydroxybenzoic acid (*p*-HBA) with acetic anhydride in the presence of the catalyst pyridine. The monomer ABA was purified by a recrystallization process in butyl acetate. AAA was also acetylated by *p*-aminophenol with acetic anhydride in a NaOH

solution at low temperatures and recrystallized from (50/50 volume) methanol/hexane. MH, TFPA, TFIA, and TFTA were purchased from Aldrich and used as received. The melting points for ABA, MH, TFIA, and TFTA are 196, 299, 212, and 275 °C, respectively, as measured by differential scanning calorimetry (Perkin-Elmer DSC Pyris 1). The following series of reaction systems were employed to study the topological defects of disclination of the surface microcracks decorated polyester films: ABA/MH/TFIA and ABA/MH/TFTA. The chemical structures for both copolyesters are shown in Figure 1.

2.2. Thin Film Polymerization. The sample preparation began with the physical mixing of the monomers and grinding them together according to a specific molar ratio to obtain a homogeneous mixture. Then, the monomer mixture was centrally placed on a microscopy cover slide. One drop of acetone was placed on the slide to dissolve the monomers. After the solvent evaporated, it left a thin layer of monomer mixture coating the glass slide. Next, the thin film layer was sandwiched between two glass slides using a 0.5 mm stainless steel ring spacer while the reactants were placed on the top cover slide.

The specimen was placed on the heating stage (Linkam THMS-600) of a PLM (Olympus BX50). The temperature was raised at 90 °C/min to the desired temperature and the time measurement was started once the desired temperature was reached. The sample was held at the desired temperature for 2 h. The PLM micrographs were further analyzed by imaging software (Image-Pro Plus 3.0). The detailed description of experimental procedures for the *in-situ* thin film polymerization has been published elsewhere.^{9,21–24}

2.3. “RIS” Metropolis Monte Carlo Method, Cerius² Computational Simulation. A RMMC (the “RIS” Metropolis Monte Carlo method) module within the Cerius² molecular simulation software for material science study was used to calculate conformational properties of polymer chains, such as persistence length, mean squared end-to-end distance, and mean squared radius of gyration. Using these properties, the RMMC program also estimates other chain properties, such as the persistence ratio and molar stiffness function of the polymer chains.²⁵ The most advanced polymeric force field, pcff (polymer consistent force field), was used for all systems. In addition to van der Waals interactions, electrostatic (Coulombic) and torsion interactions were included in the simulation. During calculations, 500 000 steps were used in the equilibrium portion while 3 000 000 steps were used in the production portion. The

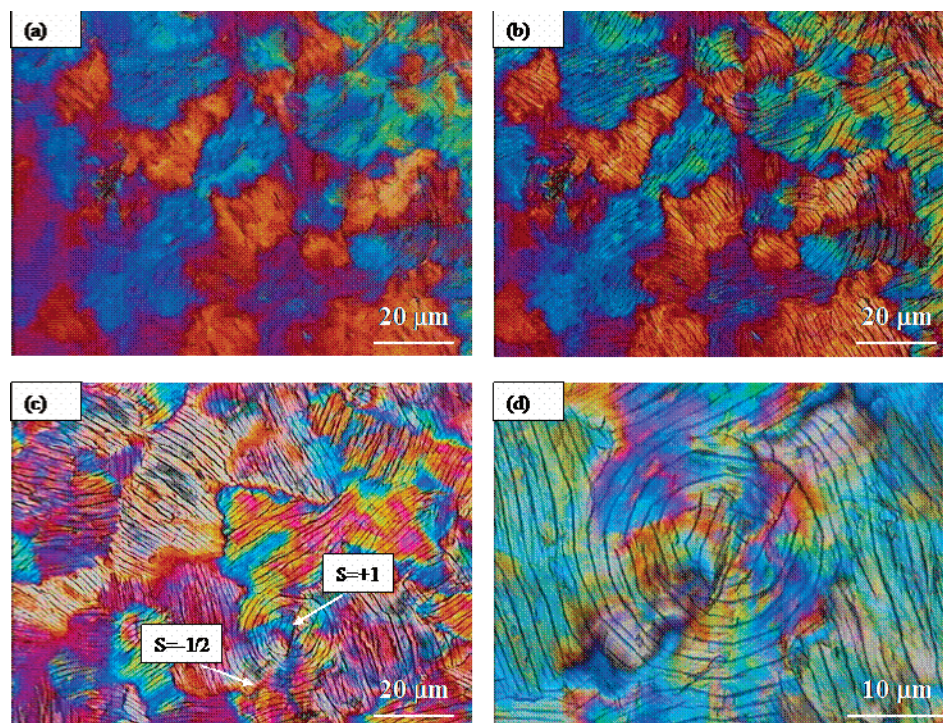


Figure 2. The morphologies of 70/15/15 ABA/MH/TFTA film at different temperatures: (a) isothermal at 300 °C for 2 h, (b) quenching to 150 °C, (c and d) the surface microcracks decoration of the integral disclination, circular pattern, $S = +1$ at room temperature.

polymers were built by the random polymer builder and the molar ratio of the simulation was 70:15:15 with 300 repeated units. Ten conformations of polymer chains were built for a particular LCPs system and the results were averaged from these calculations.

3. Results and Discussion

3.1. Disclination Defects—Surface Microcracks Decoration.

3.1.1. The ABA/MH/TFTA System. The micrographs in Figure 2a show the morphologies of the nematic-mosaic texture of the ABA/MH/TFTA film, which was polymerized at 300 °C for 2 h. After the lengthy polymerization, the thin film was quenched rapidly to room temperature. Basically, the orientation of macromolecular chains in the nematic melt can be easily frozen into a glassy nematic state and lead to surface microcracks decoration. When the sample was quenched to 150 °C, birefringence patterns and stripe patterns of anisotropic microcracks in the nematic-mosaic texture grow simultaneously, as illustrated in Figure 2b. The evolution of microcracks from the polyester main chains may produce a direct observation of LC disclination. As the quenching time increases, the surface microcracks decoration becomes sharper and more significant, suggesting that further cooling may facilitate and perfect the formation of surface microcracks with good orientation. Figures 2c and 2d show the surface microcracks decoration and resultant pattern of direction fields around disclination. From the micrographs, we observe a birefringence pattern of anisotropic microcrack, which reveals director fields of $S = +1$ and $-1/2$ disclination, and a clearer image is illustrated in Figure 2d with a higher magnification. Conversely, no disclination with $S = -1$ has been observed in this polyester film. So far, the granularity of nematic-mosaic texture evidently shows under the PLM and covers a relatively large area of the specimen, indicating the presence of a very large number of domains textures.

Taking the exiting disclination defects, for instance, the sketched map of the surface microcracks in the ABA/MH/TFTA

film is demonstrated in Figure 3. Figures 3b and 3d show the mapped molecular director orientation for domain texture and disclination with strength $S = +1$, respectively. It can be seen from the micrograph that the polymer chains are organized parallel to the microcracks direction and have a crack width of about 2 μm along the local director. These stripe patterns of anisotropic microcracks are an immediate image of molecular director fields and demonstrate the spatial distribution of the positive and negative disclinations. Generally, for each domain texture, the rigid rodlike molecules are aligned and indicated the director alignment with a high symmetry of orientation distribution. These molecules are attributed to the local director or disclination. Subsequently, the local orientated domains are aligned to present the global director orientation of LC. The total sum of the disclination strengths in a particular system should be equal to zero, which is in the most stable stage.

On the basis of the micrographs, the following observations can be made: (1) the rigid rodlike molecules are aligned with a highly symmetric axis of the orientation distribution of surface microcracks; (2) the stripes pattern of anisotropic microcracks are oriented neatly in local nematic-mosaic (domains) texture, which differ from the surrounding domains; and (3) the strength of disclination in $S = +1$ and $-1/2$ are formed in multidomain. First, the LC director alignment in each domain differs from the surrounding domains because, in an unequal constant case, different domains may have different stabilizing energies. The local director mainly comes from the alignment of the local polymer backbone. Second, the adhesion strength in each domain is comparatively high to separate the nematic-mosaic texture to an individual domain. This phenomenon is due to the ability of a single domain to transform itself to a stable state of alignment. According to Answer et al., domain is a texture that consists of rigid molecule chains in the fields' direction and bounded by walls of misorientation.²⁶ Therefore, it is well-known that this "wall" may be a big retarding factor and function as a boundary to separate a region of highly orientated molecules from others. However, the detailed nature of the boundary region

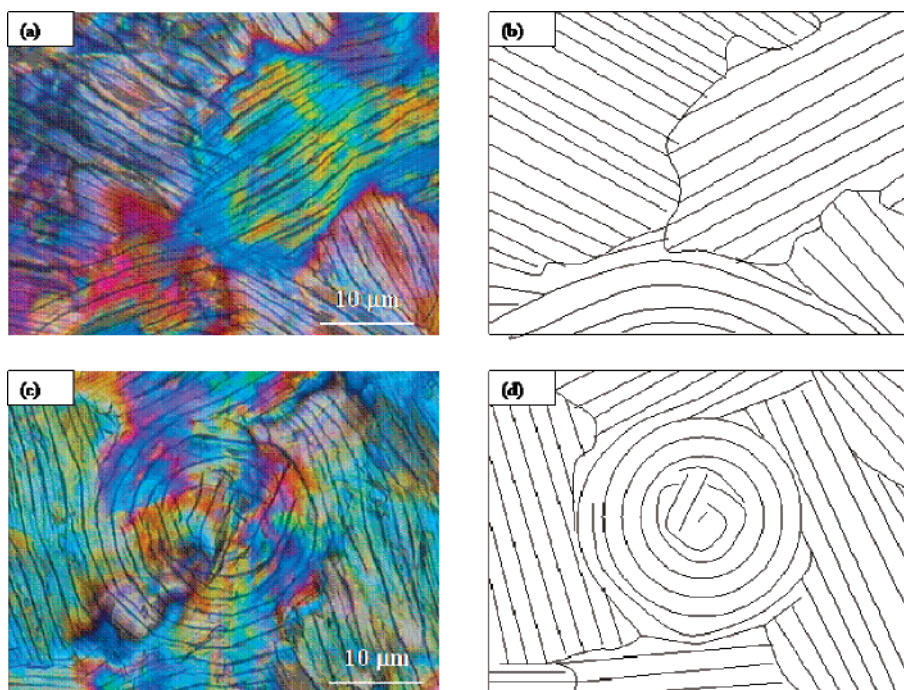


Figure 3. The surface microcracks decorated PLM micrographs for (a) domain texture and (c) disclination of $S = +1$; (b and d) the mapped molecular director orientation for a and c.

of polydomain texture is largely unknown. Last, most of the $S = +1$ and $-1/2$ disclination may defeat the defect energy in domain textures, which are just near the position of the disclination core, because evolution is promoted by the greater deformation energy during the polymerization. Another possible reason is that the disclination cores have relatively high elastic energy density and lead to a significant changes in local nematic core.²⁷ Thus, these phenomena suggest that the defect energy in the disclination core may be greater than in the single domain texture.

Although the mapping technique^{9,15,20} is applicable and popular to investigate the director field around disclination, the molecular mechanism leading to formation of surface microcracks is still unknown. Moreover, it is important to consider the feature in determining the creation of topological strength of disclination. Therefore, these factors may further complicate the fundamental study of topological defects of disclination in the LCs system. Additionally, wide-angle X-ray diffraction (WAXD) examination has been employed to characterize the chain packing in ABA/MH/TFIA films.⁸ A broad peak centered at $2\theta \sim 25^\circ$ was observed, indicating the formation of nematic nature after thin film polymerization. On the basis of the WAXD results obtained, the nematic phase is formed in the nematic-mosaic texture (nematic glassy phase). Fourier transform infrared spectroscopy (FT-IR) was employed to characterize the LCPs. The substitution of a band of an ester group after completing polymerization (about 2 h) clearly supported the formation of polyester. Moreover, the detailed in situ thin film polymerization, FT-IR characterization, and phase transition behavior of 70/15/15 mol % of ABA/MH/TFIA were discussed in our pervious study.⁸

3.1.2. The ABA/MH/TFIA System. Interestingly, a different kind of disclination defect is observed in the ABA/AAA/TFIA film. In Figure 4, ABA/AAA/TFIA, with meta-linkage, has pairs of disclination strength $S = +1$ and -1 , indicating different defect patterns of disclination as compared to the ABA/MH/TFIA system, with para-linkage (as illustrated in Figures 2 and 3). In nature, disclination tends to form in pairs with the

neighboring disclination, which has opposite strength in order to decrease the elastic distortion energy. Thus, for a pair of disclinations, an approximately equal numbers of positive and negative disclinations is frequently found in a particular system.¹⁰ Although the ABA/MH/TFIA film can exhibit $S = -1$ disclination, the $S = +1$ disclination still is the dominance disclination core observed. Hu et al. indicated that the disclination of $S = -1$ is rarely observed in liquid crystalline polymers.⁷ Hence, our result agrees well with the previous researchers that reported a disclination core.

Detailed examination of the surface microcracks decoration reveals that the ABA/MH/TFIA system tends to form disclination of strength $S = +1$ and $-1/2$, while ABA/MH/TFIA tends to develop disclination of strength $S = \pm 1$. However, both ABA/MH/TFIA and ABA/MH/TFIA systems reveal the striped microcracks decoration apart from the defects of disclination. On the basis of the micrographs obtained, the monomer structures and kink-linkages are the major concerns for the defects disclination study. Nonetheless, this is only an assumption made by the ordinary surface microcracks observation, more results from other examinations are needed to confirm and identify this hypothesis.

According to the experimental observation, there may be three different mechanisms occurring during the disclination process in our samples. First, for pairs of disclination with opposite signs ($S = +1$ and $-1/2$ in ABA/MH/TFIA and $S = \pm 1$ in ABA/MH/TFIA), they tend to attract each other in order to release the excess deformation energy and eventually form a new disclination. Obviously, this mechanism could result in annihilation of both opposite disclination signs to form a monodomain of mesophase. The second mechanism is only a disclination with strength of $S = +1$, -1 , or $-1/2$. Usually, this mechanism may lead to a smaller decrease in a defect, because they can annihilate freely without any influences from the surrounding disclination. Finally, the third mechanism is only a simple disclination in the domain texture, in which no disclination core with $S = \pm 1$ is involved in defect formation.

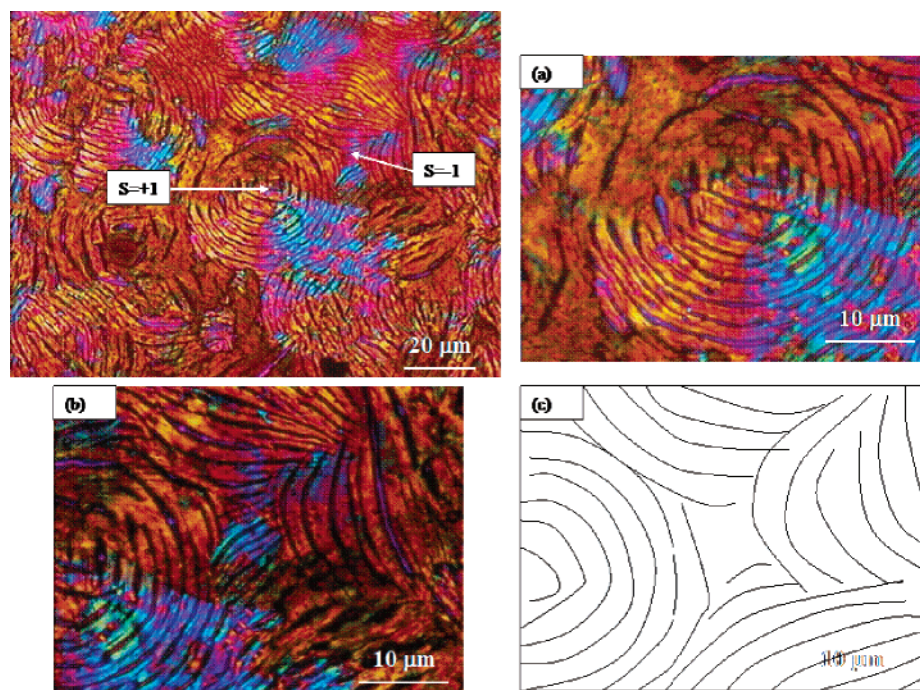


Figure 4. The surface microcracks decoration of 70/15/15 ABA/MH/TFIA of the integral disclination, circular pattern, (a) $S = +1$, (b) $S = -1$, and (c) depicted the mapped molecular director orientation for b. (c) $S = -1$.

TABLE 1: Properties of the Random Built LCPs Chains with 70/15/15 ABA/MH/(TFIA or TFTA) (300 repeated units) at the Temperature of 300 °C, Simulated by RMMC Cerius² Molecular Simulation Software

Properties of polymer chains	ABA/MH/TFIA(TFTA)	
	TFIA (<i>meta</i>)	TFTA (<i>para</i>)
Mean squared end-to-end distance (\AA^2)	83309 \pm 3950	143924 \pm 4510
Mean squared radius of gyration (\AA^2)	14356 \pm 56.5	22945 \pm 84.9
$\langle r^2 \rangle / \langle s^2 \rangle$	5.80	6.27
Persistence length (\AA)	41.07 \pm 1.56	45.27 \pm 1.84
Diameter (\AA)	5.85 \pm 0.29	4.82 \pm 0.25
Persistence ratio	7.02	9.36
Molar stiffness function ($\text{g}^{0.25} \text{cm}^{1.5} / \text{mol}^{0.75}$)	115.5	172.5

Our experimental result suggests that the third hypothesis is the most common phenomenon observed in these copolyester films.

On the other hand, we predict that the strength for $S = \pm 1$, $-1/2$ disclination in both ABA/MH/TFTA and ABA/MH/TFIA systems may be higher than the stripe pattern of microcrack in a single domain. It is possible to speculate that alignment of LC director in the stripe pattern of microcracks may suspend and/or completely cease when the reorganization energy of the molecular orientation is higher than the defect energy. In other word, the disclination strength requests greater deformation energy than the defect energy in order to present the glassy nematic phase and/or during the polymerization. Additionally, elastic constant anisotropy may be a key role in understanding the fundamental study of defect of disclination. Ford et al. reported that the curvature of the director orientation with the approached wall effects is dependent on the elastic constant of

the materials.²⁸ Moreover, Hudson et al. also indicated that the elastic constant anisotropy is high at the area very near the core of a singularity.⁶ Thus, we may conclude that the defect and reformation energies in line defects (stripe pattern of anisotropic microcracks) may be the lowest among the disclination defects.

3.2. Simulation. Table 1 summarizes the calculated results of polymers chain properties for ABA/MH/TFTA and ABA/MH/TFIA copolyesters. According to the Flory's lattice model, the critical axial ratio value of the rodlike thermotropic liquid crystallinity is 6.42.²⁹ In this study, the calculated persistence ratios for the 70/15/15 mol % ABA/MH/TFTA and ABA/MH/TFIA are 9.36 and 7.02, respectively, is evidence to prove the LC characteristics. Typically, ABA/MH/TFTA with para-linkage is predicted to have a higher persistence length and persistence ratio than the ABA/AAA/TFIA (meta) system.^{21–22,30} The simulated results do support the above hypothesis. One plausible explanation is due to the fact that the reactivity and chain

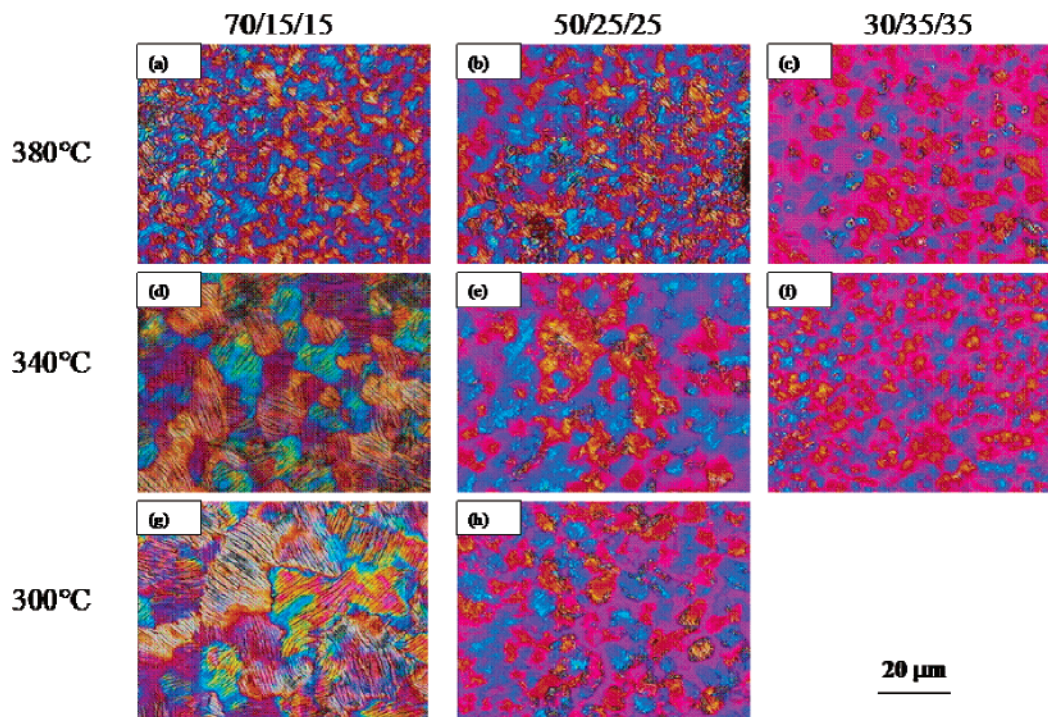


Figure 5. The surface morphologies of ABA/MH/TFTA at different monomer compositions and reaction temperatures.

straightness of TFTA are higher than those of TFIA units, which may result in some bulkiness in the polymer chain. Additionally, the chain orientation and packing are prevented to some extent by two symmetrical carbonyl groups that are present in the linear TFTA unit, indicating a greater degree of linear symmetry and higher packing density in ABA/MH/TFTA system. The incorporation of the TFIA (meta) unit can effectively reduce 33% of the molar stiffness function and 7% of the persistence length as compared to the TFTA (para) system. These phenomena provide evidence that the lower intramolecular attractive force and high polarity in meta-linkages may disturb the stability of the LC phase.

For further understanding the spatial characteristics of polymer chains, our calculated simulation results (value of $\langle s^2 \rangle$ and $\langle r^2 \rangle / \langle s^2 \rangle$) may provide additional insight for intermolecular adhesion study. Attaching a meta-linkage to the molecular rigid backbone is a means to reduce the regularity of a molecule and decrease the melting temperature.⁴ The incorporation of the TFIA (meta) unit can effectively reduce 37% of the dynamic mean-squared radius of gyration ratio ($\langle s^2 \rangle$) compared to the ABA/MH/TFTA system. This may be plausibly due to the excess electronegative fluorine charge in the meta-linkage, resulting in an increase in the interstitial space among polymer chains. Yet, the meta-linkage tends to introduce the wormlike polymer chains in the rigid-rod backbone. On the other hand, the value of $\langle r^2 \rangle / \langle s^2 \rangle$ can be used to characterize the linearity of polymer; the higher the $\langle r^2 \rangle / \langle s^2 \rangle$ value, usually the more linear the polymer chain. The calculated $\langle r^2 \rangle / \langle s^2 \rangle$ values increases from meta- to para-linkage, indicating that the rigid meta system may form a wormlike structure and yet reduce the chain linearity.

3.3. Effect of Reaction Temperature and Monomer Composition. Figures 5 and 6 display the effect of reaction temperatures (300, 340, and 380°C) and monomer compositions (70/15/15, 50/25/25, and 30/35/35 mol %) on surface microcracks decoration in ABA/MH/TFTA and ABA/MH/TFIA films. Before discussing the influence of reaction temperature and monomers composition for surface microcracks evolution, it might be helpful to consider the various factors of mesophase

formation, such as liquid crystallinity, polymers linearity, regularity, and rigidity (kinks effect in our study). Generally, the formation of a mesophase is the essential tool to develop surface microcracks decoration. Thus, the ordered domain texture will grow in size during polymerization and readily form microcracks during quenching. On the basis of these micrographs, microcracks can develop when the domains form and reach an adequate size.

The effect of reaction temperature on the formation of surface microcracks is a complicated study, because it comprises several competitive factors. For both copolymers system, the relatively higher melting points of MH and TFTA require high enough polymerization to produce high molecular weight copolymers and randomly distribute along the copolymer chain. Basically, three hypotheses can be drawn from the PLM results: (1) liquid crystalline system with a higher molecular weight has higher deformation energy for a similar disclination density and (2) the viscosity of the liquid crystalline systems with the same molecular weight is lower at a relatively higher temperature. Hypotheses 1 and 2 are generally favorable for annihilations, leading to a decrease in the number of disclinations and enlargement of the domain areas/size. However, (3) for a comparatively higher polymerization temperature, the polymerization process reacts quickly and the viscosity of the polymerization system increases rapidly. For hypothesis 3, the texture with a lower disclination density cannot be fully developed. This phenomenon leads to formation of small domains, which is unfavorable for the formation of surface microcracks. The overall effect of reaction temperature on the formation of surface microcracks is a combination of these competitive factors. The 70/15/15 ABA/MH/TFTA, 70/15/15 ABA/MH/TFIA, and 50/25/25 ABA/MH/TFIA systems are most likely dominated by hypothesis 3. On the other hand, the 30/35/35 ABA/MH/TFTA system is subjected to hypotheses 1 and 2.

As compared to the 50/25/25 mol % ABA/MH/TFTA, 70/15/15 mol % ABA/MH/TFTA shows a clearer microcracks decoration and relatively larger domain size at the same reaction

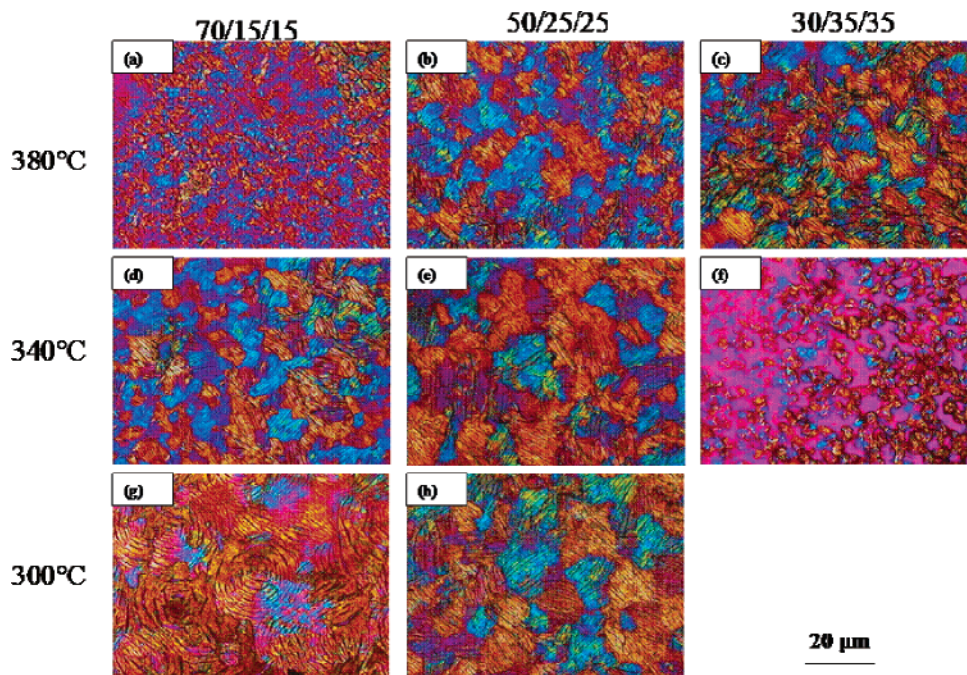


Figure 6. The surface morphologies of ABA/MH/TFIA at different monomers composition and reaction temperatures.

temperatures. By further decreasing the ABA content, the domain area/sizes reduce dramatically. A similar trend of reduction in domain size is also observed in the ABA/MH/TFIA system, as demonstrated in Figure 6. Although both simulation and experimental confirmed the ABA/MH/TFTA (para) and ABA/MH/TFIA (meta) systems for formation of surface microcracks, interestingly, the former system requires a much lower critical ABA content for formation of surface microcracks than the latter. Only 70/15/15 mol % ABA/MH/TFTA can show the surface microcracks at various reaction temperatures, whereas 30/35/35 mol % ABA/MH/TFIA was still able to form the surface microcracks at 380 °C. This may be due to the fact that TFIA (212 °C) monomer has a lower melting point than TFTA (275 °C), hence possessing a higher ability for polymerization. Moreover, the simulation results (as tabulated in Table 1) suggest that the chain conformations of the ABA/MH/TFIA system are strongly affected by TFIA monomer units. In this case, the ability to form surface microcracks is greater in the ABA/MH/TFIA system, probably due to the intermolecular crack, which describes the variation of un-deformed molecules in the director fields. This result is consistent with the $\langle s^2 \rangle$ result that the lateral interchain cohesion in the ABA/MH/TFIA system is relatively weak. Hence, the surface microcracks decoration also can be observed in a higher TFIA content.

In addition, crystallization may be a retardant for mesophase and furthermore for formation of surface microcracks. For some LCPs, the crystal structure will grow in nematic LCs phase during the polymerization, implicating that the crystalline texture is more stable than the mesophase. Figure 6f demonstrates the micrograph for 30/35/35 mol % ABA/MH/TFIA, which reacted at 340 °C, with the crystal texture visibly formed in the film. On the basis of the results obtained, it can be deduced that the crystallization significantly affects and prohibits the formation of surface microcracks. From both simulation and experimental data, there is clear evidence that monomeric structures (ABA, MH, and TFIA and TFTA, which represent the polymer chain regularity, linearity, and rigidity) and reaction temperature play an important role in mesophase and formation of surface microcracks.

4. Conclusions

Both ABA/MH/TFTA (para) and ABA/MH/TFIA (meta) films form surface microcracks decoration in nematic-mosaic texture during a rapid quenching. Disclination with strength $S = +1$ and $-1/2$ are observed in the ABA/MH/TFTA film, while both $S = \pm 1$ have been exhibited in the ABA/MH/TFIA system. Apart from these disclination, the molecular director fields in nematic-mosaic textures have line defects (stripe pattern of anisotropic microcracks) in both films. The weak lateral interchain cohesion may introduce microcracks more easily. PLM analysis also indicates that the polymer chain regularity, rigidity, linearity, and monomeric units distribution and composition affect the mesophase and formation of surface microcracks. From RMMC results, both systems exhibit a persistence ratio larger than 6.42, which satisfies the minimum requirement for the LCs formation.

Acknowledgment. The authors would like to thank NUS for funding this research with grant number R-279-000-176-112. Thanks are also due to the Institute of Materials Research and Engineering (IMRE) for the equipment. Special thanks are given to Ueno, Teijin, and Sumitomo Chemicals for their provision of monomers. The authors also thank Ms. Shen Lu for various assistance in operating characterization instrument and equipment.

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