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Thin-film polymerization and characterization of Sumitomo's Sumikasuper[®]-type liquid crystalline polymers

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Using the thin film polymerization approach, we have studied the texture evolution when synthesizing a novel liquid crystalline polymer (LCP) system based on Sumikasuper[®] LCPs. The main monomers used were *p*-acetoxybenzoic acid (ABA), 4,4'-biphenol (BP), isophthalic acid (IA), phthalic acid (PA) and terephthalic acid (TA). Polarizing optical microscopy (POM), FTIR, X-ray diffraction (XRD) and atomic force microscopy (AFM) were employed to study the thin film polymerization process and characterize the products. The generation and evolution of liquid crystal phases were monitored; the results revealed that there exists a composition range for the monomers to react and form liquid crystal materials. The critical temperature for LC formation in ABA/BP/IA system decreased with increasing ABA content. FTIR results confirmed the formation of polymers. AFM investigation suggested a similar process of morphological change to that observed using POM. An increasing surface roughness of the thin films with the progress of polymerization was also obtained from AFM analysis. A nematic LC texture of the polymer system was suggested by XRD examination. Results obtained by replacing BP with acetylated BP, and by conducting polymerization using two-monomer systems, suggest that BP units are included in polymers obtained by the thin film polymerization method.

1. Introduction

During the last two decades a new class of polymeric materials has been developed and has received much attention from both industry and academia. These materials are liquid crystal polymers (LCPs). They have the characteristics of conventional liquid crystals (LCs) used in electronic display devices except for a much higher molecular mass, a difference that provides unique features. Especially important is the existence of a glass transition point which permits the freezing of a LC phase for use over a wide range of temperature, thus yielding thermal, mechanical and optical properties superior to those of conventional thermoplastics.

The first company to commercialize tractable, wholly aromatic thermotropic polyesters and poly(ester-amide)s was Celanese with the trademark 'Vectra' in the early 80s, based on the composition of Calundann *et al.* [1, 2].

Since then, the LCP field has grown substantially and today more than seven companies have thermotropic LCP products. Comprehensive progress reviews on LCP research and development have been carried out by both academia and industry [3–12].

Sumitomo's Sumikasuper[®] LCPs are a variety of recently commercialized LCPs. This type of thermotropic LC polyesters was the first commercially produced LCP in Japan [13]. They exhibit extremely high heat resistance and performance superiority. Surprisingly, to the best of our knowledge, there are few academic studies of this new LCP material [14–15]. The many impressive properties of this new material, were an incentive to study the fundamentals of its synthesis.

Sumikasuper[®] LCPs comprise the following basic monomeric units: *para*-hydroxybenzoic acid (*p*-HBA), biphenol (BP) and one or more of phthalic acid (PA), isophthalic acid (IA) and terephthalic acid (TA), as shown in figure 1 [13]. Sumikasuper[®] LCP is, in fact, a modified

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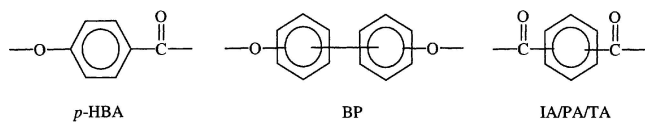


Figure 1. The monomeric units in Sumikosuper[®] LCPs.

variant of Xydar (Dartco) that is composed of HBA, BP, and TA [2, 3, 8, 10, 11, 16–18]. The incorporation of IA or PA results in kinks in the main chain and lowers the melting point, allowing easy melt processing.

Although this series of polymers has been commercialized, some fundamental issues regarding their synthesis and characterization are still not well understood. For example, what are the key factors that determine the properties of this type of LCP, and how do these key factors (such as monomer structure and reaction temperature) influence the end use properties and liquid crystallinity of the resultant polymers. To this end, we have employed the thin film polymerization approach to study the Sumikasuper[®] LCP system. The thin film polymerization technique is a very simple and powerful tool for investigating the fundamental synthesis issues in LCPs. It is a quick and convenient method because it consumes extremely small amounts of monomers and the reaction temperature can be accurately controlled.

Rybnikar *et al.* [19, 20] studied the thin film polymerization of various LCPs by sandwiching monomers between two glass slides; these were wrapped with aluminum foil before placing on a hot plate to initiate the thin film polymerization reaction. Cheng and Chung advanced the thin film polymer technique by conducting the reaction on a polarizing microscope with a novel sample assembly [21–24]. The advantage of their work is the *in situ* monitoring of the evolution of LC morphological changes during the polycondensation reaction. In this report, we extend the same method to the study of a novel LCP system based on Sumikasuper[®] LCPs, which comprise *p*-HBA, BP (or 4,4'-diacetoxybiphenyl, DABP), IA (and/or PA and TA), monomeric units. Our purpose was to determine the composition range for LC formation and to examine the LC texture generation and evolution during the polymerization process. The influences of monomer structure and reaction temperature on the texture appearance of the ABA/BP/IA LCP were also investigated.

2. Experimental

2.1. Materials

The main monomers used were *p*-acetoxybenzoic acid (ABA), 4,4'-biphenol (BP), and isophthalic acid (IA). In order to examine the influence of monomer structure on the reaction process and the product, we also employed 4,4'-diacetoxybiphenyl (DABP) to replace BP and phthalic acid (PA) to replace IA or TA in the reaction system. While BP, IA, TA and PA were purchased from Aldrich

and used as received, ABA and DABP were acetylated from *p*-HBA (Teijin, Japan) and BP, respectively, according to literature reports [21, 23, 25]. The success of acetylation was confirmed by ¹H NMR spectroscopy. The melting points of *p*-ABA, BP, DABP, PA, and IA are 196, 282, 163, 205 and 342°C, respectively, as tested by DSC (Perkin Elmer DSC Pyris 1). TA decomposes before melting temperature is reached. Their chemical structures are shown in figure 2.

2.2. Thin film polymerization

The compositions studied in this work were as follows:

- (1) ABA/BP/TA, ABA/BP/IA and ABA/BP/PA at a 70/15/15 molar ratio; and ABA/BP/TA/IA at a 70/15/7.5/7.5 molar ratio.
- (2) ABA/BP/IA: 90/5/5; 80/10/10; 70/15/15; 60/20/20; 50/25/25; 40/20/20; 30/35/35; 20/40/40 and 10/45/45; and the 70/15/15 ABA/DABP/IA system.

Monomers with a particular molar ratio were mixed and ground into a fine powder. About 2 mg of the monomer mixture was placed on a glass slide, then several drops of acetone were deposited on the glass slide to dissolve the monomers. After evaporation of the solvent, a thin layer of the reactant mixture remained attached to the glass slide and was then sandwiched against an additional glass slide with a ring spacer. The ring spacer provided space for easy removal or release of acetic acid during polymerization. Without the spacer, it was found that reproducibility was quite low and film quality was poor because the evaporation (or release) of acetic acid at elevated temperatures was vigorous. The monomers were attached to the top slide.

The whole package was placed on the heating stage (Linkam THMS-600) of a microscope and heated to a proposed temperature with a heating rate of 90°C min⁻¹. The sample was held at that specific temperature during the

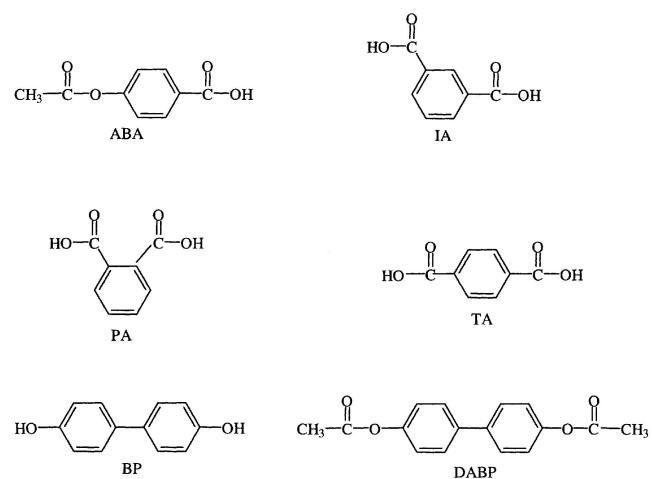


Figure 2. The monomers used in the thin film polymerization.

whole reaction process. When the heating stage reached the proposed temperature, recording of the reaction time was begun. The temperature of the top slide was calibrated by measuring the melting points of the pure monomers as well as by measuring with a thermocouple. The polymerization was carried out on the top slide and all the temperatures mentioned refer to the temperature of top slide. The reaction process was observed *in situ* by POM using an Olympus BX 50 with crossed polarizers, between which a red plate having the retardation of 530 nm could be inserted. The micrograph data were analysed by an imaging software (Image-Pro Plus 3.0).

2.3. FTIR characterization

The FTIR spectra of the monomers and polymers at different reaction times were recorded on a Perkin-Elmer Spectrum 2000 FTIR Spectrometer. The polymers obtained by thin film polymerization were scraped carefully from the glass slides with no further treatment and prepared as KBr pellets for IR measurement.

2.4. Atomic force microscopy

Investigation of the surface morphology and roughness of the thin film copolymers was conducted on a ThermoMicroscope Autoprobe CP Research AFM system, from Park Scientific Instrument, Sunnyvale, CA, in a contact mode. Conical silicon tips mounted on a silicon cantilever with a force constant of 0.26 to 2.1 N m⁻¹ were employed. The silicon cantilevers (with an integral tip) had a length of 180 or 85 μm, width of 18 to 38 μm, thickness of 1 μm and resonant frequency of 40 to 160 kHz. The images presented contain 512 × 512 data points. The surface topographical images were processed using IP2.1 image software provided by the supplier.

Roughness measurements can be performed over an entire image or a selected portion of the image. The most common measurements are the root mean square (rms) [26, 27]. The rms roughness (R_q) is defined as the standard deviation of the height values within the given area:

$$R_q = [\sum(Z_i - Z_{ave})^2/N]^{1/2}$$

where Z_{ave} is the average of the Z values within the given area, Z_i is the Z value for a given point, and N is the number of the points within the given area. The thin film copolymer surfaces were imaged over a scan area of 50 × 50 μm² by a contact mode. At least three different locations were scanned and the RMS roughnesses were averaged to give the sample roughness.

2.5. X-ray diffraction

Wide-angle X-ray diffraction experiments were performed at room temperature with a Bruker X-ray diffractometer in the reflection mode with a graphite

monochromator and a Cu Kα radiation (λ 1.5418 Å). The samples were prepared from the 70/15/15 ABA/BP/IA system reacted at 380°C for 60 min on silicon substrates and at 300°C for 30 min on glass substrates. Although most thin film polymerizations were carried out on glass substrates, we also employed silicon as a substrate for the XRD investigation because silicon is a single crystal and has only one fixed XRD peak at about 28° (2θ). It has been confirmed by PLM that the thin-film product on the silicon substrate has the same LC texture as that on the glass substrate. The LC image of the sample on the silicon substrate was observed by a reflection mode through PLM, while that reacted on the glass substrate was observed by a transmission mode.

3. Results and discussion

3.1. The ABA/BP/PA, ABA/BP/TA, ABA/BP/IA and ABA/BP/TA/IA systems

Figure 3 illustrates a comparison of the effects of *ortho*-, *meta*- and *para*-linkages on the evolution of morphological changes and liquid crystallinity. The 70/15/15 molar ratio was chosen because this composition is very close to commercial compositions [13]. At least two factors affect the formation of liquid crystallinity and texture evolution: namely, configuration of a linkage and reactivity of a monomer. Since IA, PA and TA have an *ortho*-, a *meta*- and a *para*-linkage, respectively, the incorporation of IA or PA creates kinks and disturbs the straightness of the resultant polymer chains; TA maintains chain straightness but has a low reactivity because of its high melting point.

Figures 3(a) and 3(b) show that PA has a slightly higher tendency to form liquid crystallinity than IA. Liquid crystallinity in the ABA/BP/PA system appears earlier (111 s) than in the ABA/BP/IA system (179 s). Two possible reasons for this interesting phenomenon are (1) PA has a much lower melting point than IA (205 vs 342°C); (2) the ABA/BP/PA system may form a polymer with a spiral chain configuration because of the rotation of bridging groups [24]. A similar phenomenon was reported by Cheng and Chung [24] when studying the ANA/AAA/PA and ANA/AAA/IA systems. ANA/AAA/PA has a higher tendency to form a LC than ANA/AAA/IA, while the latter yields a much more stable LC phase than the former.

Because of the high melting point of TA, polymerization of the ABA/BP/TA system cannot yield totally random copolymers. The liquid crystal phase appears before all TA crystals disappear, indicating that TA has a low reactivity at this temperature. It can be seen from figures 3(c) and 3(d) that the introduction of TA into the reaction system almost prevents LC growth even though it can be observed. The system ABA/BP/IA/TA 70/15/7.5/7.5, figure 3(d), apparently does not improve the situation significantly.

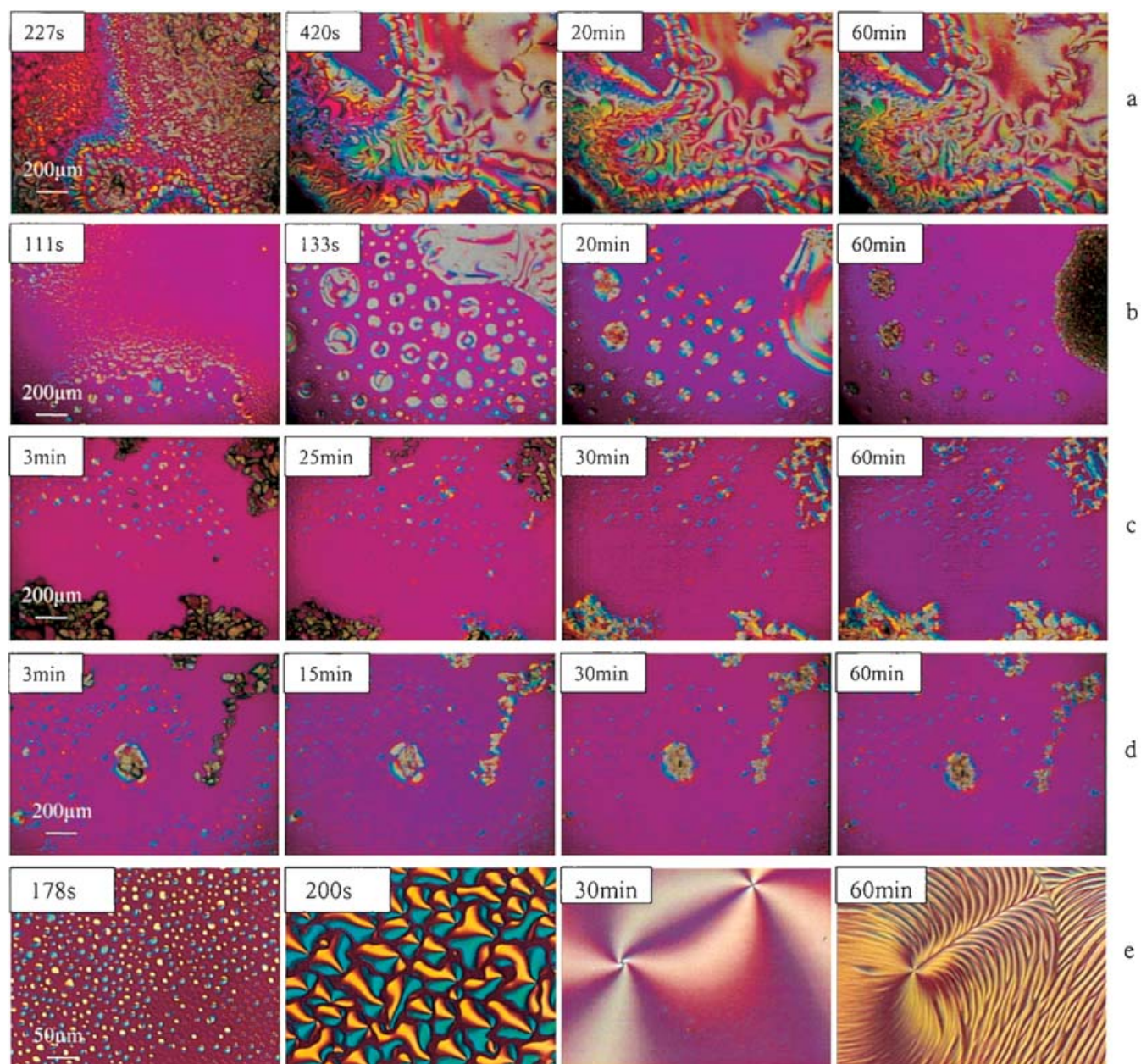


Figure 3. Micrographs showing the morphological changes of different reaction systems: (a) 70/15/15 ABA/BP/IA at 380°C, (b) 70/15/15 ABA/BP/PA at 380°C, (c) 70/15/15 ABA/BP/TA at 380°C, (d) 70/15/7.5/7.5 ABA/BP/IA/TA at 380°C and (e) 73/27 ABA/ANA at 250°C. With the same magnification, micrographs were obtained from the same area of each sample.

When comparing the above systems to the Vectra reaction system (73/27 ABA/2,6-acetoxynaphthoic acid) [21, 22], the Sumikasuper system shows relatively low tendency to LC formation than the Vectra system in the temperature range studied. It can be seen clearly from figure 3(e) that liquid crystallinity in the Vectra system appeared early and developed very quickly. All monomers melted before the formation of liquid crystal droplets and typical schlieren and banded textures could be observed clearly. This is because Vectra employs lower melting point

and straight configuration monomers (226 and 196°C for HNA and HBA, respectively), which favours the formation of liquid crystallinity; while the Sumikasuper monomers have a broad melting point range and contain many kinks.

3.2. The ABA/BP/IA system

To determine the critical IA content for this system to yield liquid crystallinity, the ABA content was varied from 0% to 100% while BP and IA were kept at the same molar ratio in each composition, as required by

stoichiometry for the formation of polymer instead of oligomer. For the system with low ABA contents, i.e. 20/40/40 and 30/35/35 ABA/BP/IA, no LC phase was formed at the temperatures examined (300, 320, 340 and 360°C). For example, for ABA/BP/IA 20/40/40 the monomer crystal mixture melted completely at 360°C within 10 min, but LC phase formation was not observed even after the reaction system was kept at 360°C for 1 h.

When the ABA content in the ABA/BP/IA reaction system was increased, i.e. higher than 40%, a well developed LC phase was observed. One example is shown in figure 4 for the 80/10/10 ABA/BP/IA composition at a reaction temperature of 320°C. The micrographs show the morphological change of the reaction system during thin film polymerization; the generation, time evolution and formation of liquid crystal texture are displayed. At the start of polymerization, LC domain was formed alongside the unmolten monomers with the formation of oligomers. Chain growth of the oligomeric molecules and combination of the LC domains lead to the formation of a nematic schlieren texture. However, the LC schlieren texture appearance was accompanied by a high density of defects. Then, annihilation between defects occurs to

release the excess of energy, resulting in a decrease in the number of defects in the reaction system. With increasing reaction time, solidification takes place and a texture, which is likely a banded texture, begins to form. After about 30 min, the view is full of the band-like texture. There is little change in texture for longer (120 min) reaction time.

For the same composition, a higher reaction temperature usually leads to easier and faster formation of the LC phase. This can be seen from the micrographs of figure 5, where reactions were carried out at 260, 300, 320 and 340°C, respectively, for the ABA/BP/IA 80/10/10 composition. At 260°C, the monomers take a long time (about 70–80 min) to melt and react. No solidification is observed even after a 3 h reaction time. However, when the reaction temperature is increased to 300°C, monomer melting and polymerization take place earlier and the reaction mixture begins to solidify after about 1 h reaction time. With the increase of reaction time, a typical schlieren texture is developed. For the reaction temperatures 320°C and 340°C, solidification occurs after 1 h and 40 min, respectively. This is understandable, as a higher reaction temperature provides more energy for the activation of

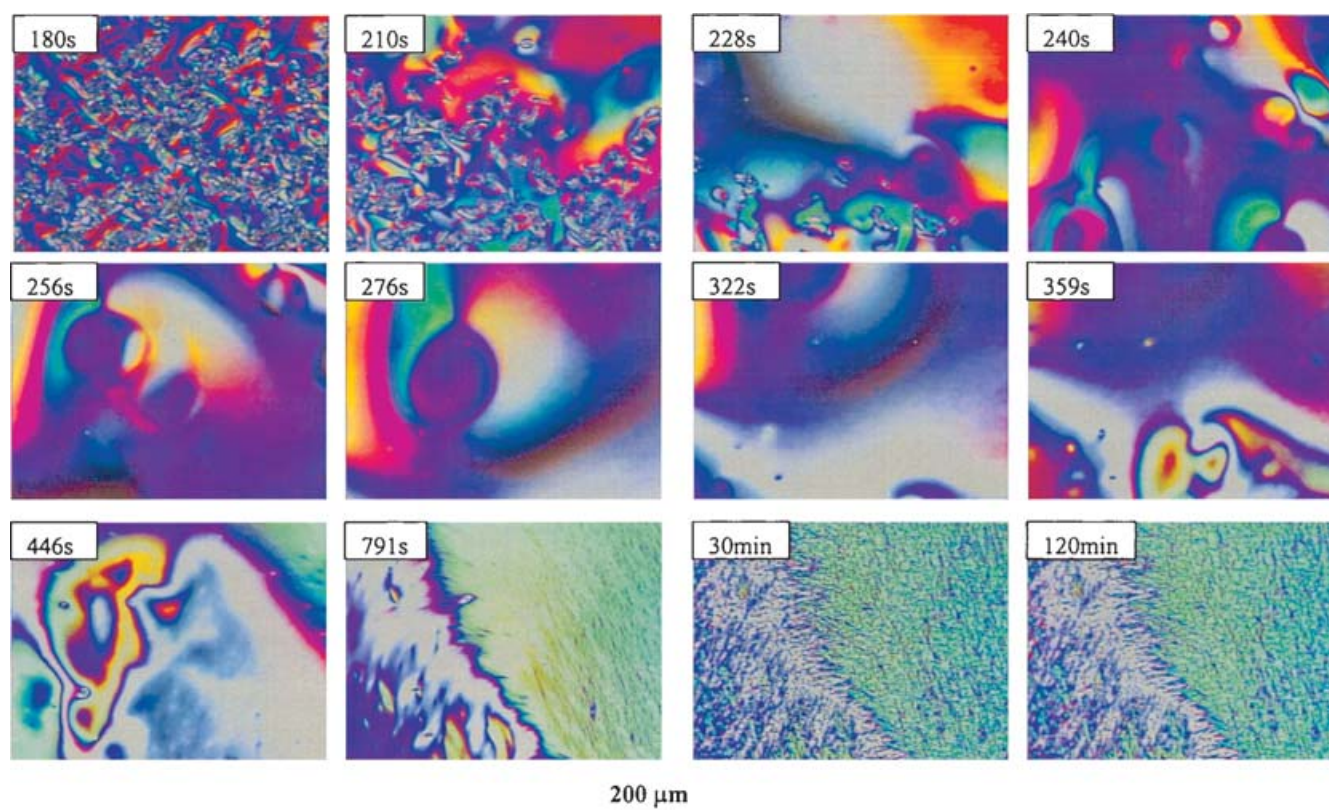


Figure 4. Micrographs showing the morphologies of the reaction system ABA/BP/IA 80/10/10 at different reaction times during thin film polymerization. All the micrographs were obtained from the same area of the same sample; reaction temperature was 320°C.

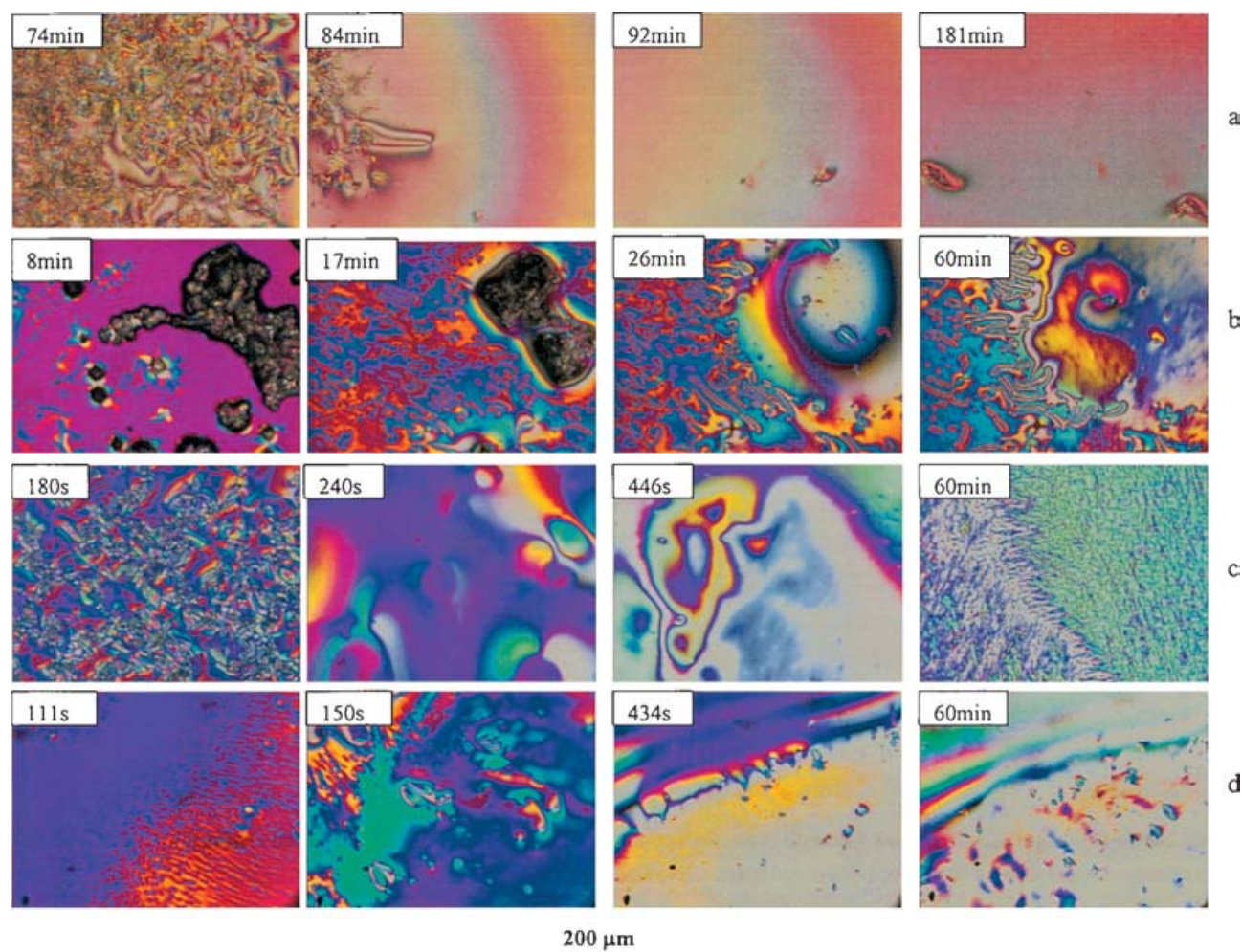


Figure 5. Micrographs showing LC texture evolution for the 80/10/10 ABA/BP/IA polymerization reaction system at different reaction temperatures: (a) 260°C, (b) 300°C, (c) 320°C and (d) 340°C. All the micrographs were obtained from the same area of the same sample.

monomers, polycondensation among monomers and chain growth of oligomeric/polymeric molecules. A higher temperature also facilitates faster movement and annihilation of disclinations. Another possible reason is the increase in melting point of the polymeric product with increasing backbone chain length during the thin film polymerization process. The polymeric/oligomeric molecules produced after a certain reaction time exhibit liquid crystallinity only at temperatures above their melting points. Therefore, for polymeric/oligomeric molecules with the same chain length, liquid crystallinity cannot be observed at lower temperatures, but is seen at higher temperatures.

Monomer composition also exerts a strong influence on the generation and evolution of LC phases. The higher the ABA content, the shorter the reaction time required for the formation of an LC phase and the better its development. This is shown by the difference in reaction time

and morphology exhibited in figure 6 for different ABA contents. A lower ABA content means a higher IA content. IA is extensively employed in LCP synthesis as a modifying monomer to lower the melting points of LCPs, because it introduces kinks into molecular chains. However, the kink, or the *meta*-linkage, also disturbs liquid crystallinity if its content is too high.

ABA/BP/IA 40/30/30 is the critical composition for the formation of an LC phase in the ABA/BP/IA system. However, at this composition the LC phase did not always appear in repeated experiments; this may be due to a critical characteristic of this composition. The formation of an LC phase at this composition may be strongly influenced by the environment or slight differences in handling when the reaction system is packed.

For the ABA/BP/IA system above the critical composition, the critical temperature for LC phase generation is different. Figure 7 shows the critical temperatures for

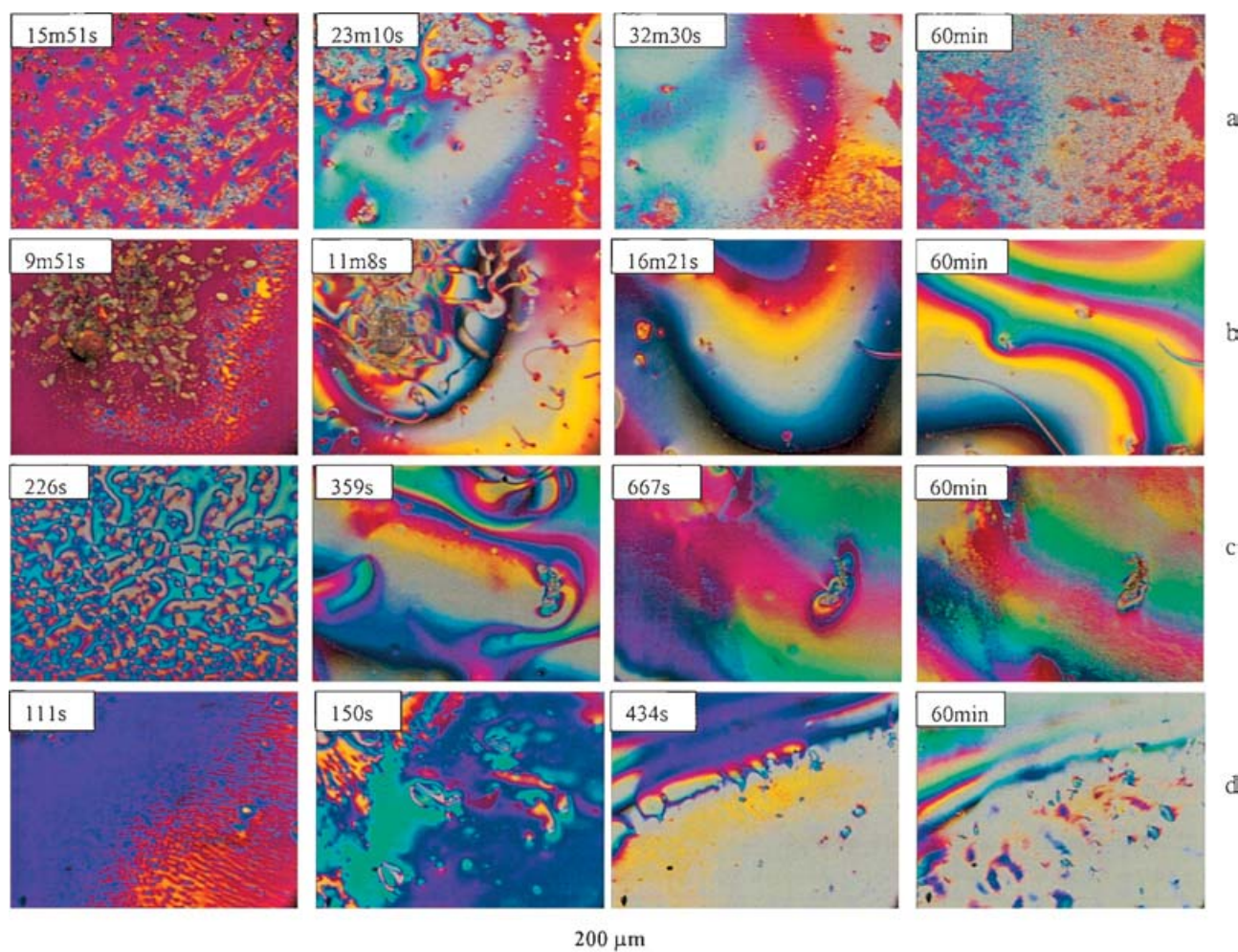


Figure 6. Micrographs showing LC texture evolution for the ABA/BP/IA polymerization reaction system with different ABA content: (a) 40 mol %, (b) 50 mol %, (c) 60 mol % and (d) 80 mol %. All the micrographs were obtained from the same area of the same sample; reaction temperature was 340°C.

the ABA/BP/IA reaction system with varying ABA content. It can be seen that with increase of ABA content, the critical temperature decreases. The main reason may be the different kink contents and the different melting points among the monomers. The melting points of ABA, BP and IA are 196, 282 and 342°C, respectively, and a higher ABA content means lower BP and IA contents. When the system contains more ABA, a lower temperature is sufficient to melt the mixture of monomers although the time required is longer, as shown in figure 5(a). After the monomers melt, they have more chance to interact with each other than in solid state.

Other explanations for the above observation may be: (1) reactions taking place at different temperatures and lasting for different durations may yield different lengths of monomeric units in the polymeric/oligomeric chains; (2) oligomers may tend to solidify at a low temperature but exhibit liquid crystallinity at a higher temperature.

3.3. FTIR characterization and inherent viscosity measurements

The occurrence of polycondensation and transesterification among the monomers during thin film polymerization was confirmed by FTIR spectra. For the ABA/BP/IA system, there are three types of reactive groups among the three monomers. They are carboxyl ($-\text{COOH}$), acetyl ($\text{CH}_3\text{COO}-$) and hydroxyl ($-\text{OH}$). When the monomer mixtures were heated during thin film polymerization, both transesterification between carboxyl and acetyl groups and etherification between carboxyl and hydroxy groups occur, with the elimination of acetic acid and water.

By monitoring the change in the absorption peaks of acetyl, hydroxyl and carboxyl groups in the IR spectra, we can obtain information on the thin film polymerization reaction. Figures 8(a–d) illustrate the FTIR spectra of the thin film copolymers of the 70/15/15 ABA/BP/IA

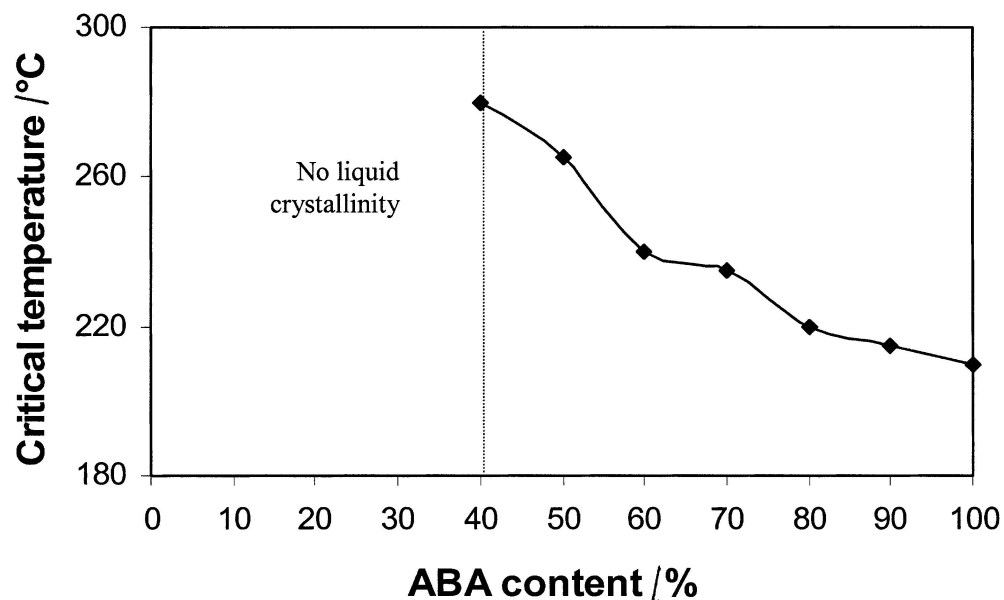


Figure 7. Critical temperatures for different compositions of the system ABA/BP/IA.

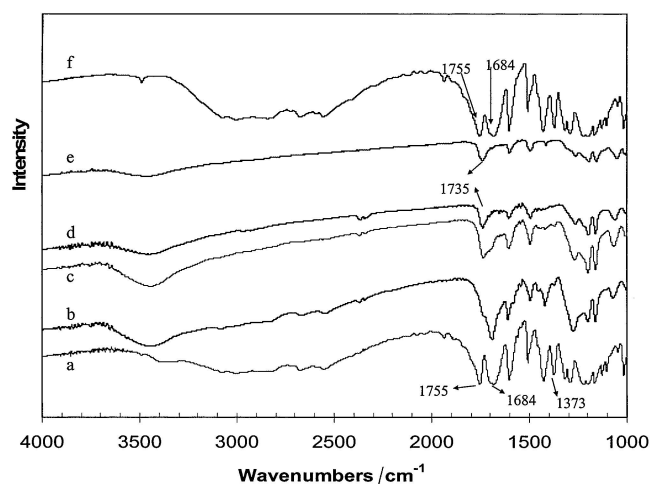


Figure 8. FTIR spectra of the 70/15/15 ABA/BP/IA reaction system at 300 °C for different times: (a) 0 min, (b) 4 min, (c) 10 min, (d) 60 min; and of the 70/15/15 ABA/DABP/IA reaction system at 300 °C for: (e) 60 min and (f) 0 min.

system after reacting for 0, 4, 10 and 60 min. In the spectrum of the monomer mixture (a), the bands at 1684 and 1755 cm^{-1} are assigned to $\nu_{\text{C=O}}$ of $-\text{COOH}$ and $\text{CH}_3\text{COO}-$ groups, respectively. The broad band in the range 2200–3200 cm^{-1} is attributable to $\nu_{\text{O-H}}$ of carboxyl and $\nu_{\text{C-H}}$ of acetyl, while the band at 1373 cm^{-1} is $\delta_{\text{C-H}}$ of acetyl. The band at about 3370 cm^{-1} is assigned to the $\nu_{\text{O-H}}$ of the hydroxy group in BP. After reacting for 4 min (b), the intensities of the bands at 1684, 1755, 1373, 3370 cm^{-1} and the broad band at 2200–3200 cm^{-1} decrease greatly, when the LC phase begins to form alongside the unmolten monomers. With an increase in reaction time (c), the intensities of these bands decrease

gradually while the band at 1735 cm^{-1} increases gradually, indicating that the reactions between carboxyl and acetyl/hydroxyl take place continuously. When the reaction time is 60 min (d), i.e. after the full development of the banded texture, the bands at 1684, 1755, 1373, 3370 cm^{-1} and the broad band at 2200–3200 cm^{-1} almost completely disappear, while that at 1735 cm^{-1} becomes very strong, indicating the formation of a substantial amount of ester groups.

The results from FTIR spectra suggest that the OH groups from both phenol and carboxylic acid, as well as the acetyl, have disappeared and the copolymer has been synthesized after 60 min reaction time. The thin film polymerization product of the 70/15/15 ABA/BP/IA system has a similar FTIR spectrum to that of the commercial product Sumikasuper[®] LCP4000.

The inherent viscosity (IV) of both thin film polymerized Vectra 72/27 ABA/ANA and Sumikasuper[®] 70/15/15 ABA/BP/IA systems were tested. The value for the 72/27 ABA/ANA system is about 2.7, which is regarded as acceptable because the IV range for that LCP should be 2.6–6.5, as mentioned in the US patents [1]. However, the 70/15/15 ABA/BP/IA system does not dissolve in common solvents, or in solvents commonly used for LCPs such as 3,5-bis(trifluoromethyl)phenol (BTMP) and pentafluorophenol (PFP).

3.4. Roughness (rms) of 70/15/15 ABA/BP/IA thin film copolymers

The AFM topographical images of thin film surfaces of the 70/15/15 ABA/BP/IA system after reacting for 5, 6, 15, 30 and 60 min at 300 °C were recorded. Three different locations were scanned for each sample and

one each for 5, 6 and 60 min are presented in figures 9(a–c), respectively. The table shows the corresponding rms surface roughness values (R_q) obtained for the thin film copolymers at different reaction times. The table shows that the rms roughness value increases from 9 nm at 5 min to 88 nm at 60 min.

According to results obtained from POM, the sequence of the morphological changes in thin film polymerization

is as follows: (1) generation of LC phase alongside the un-molten monomers (e.g. from the beginning to 4–5 min); (2) formation of the schlieren texture (e.g. from 6 min to 40 min); (3) development of the band-like texture and/or solidification (e.g. from 1 h to 2 h). The AFM images obtained at different reaction times seem to suggest a similar process occurring, as shown in figure 9.

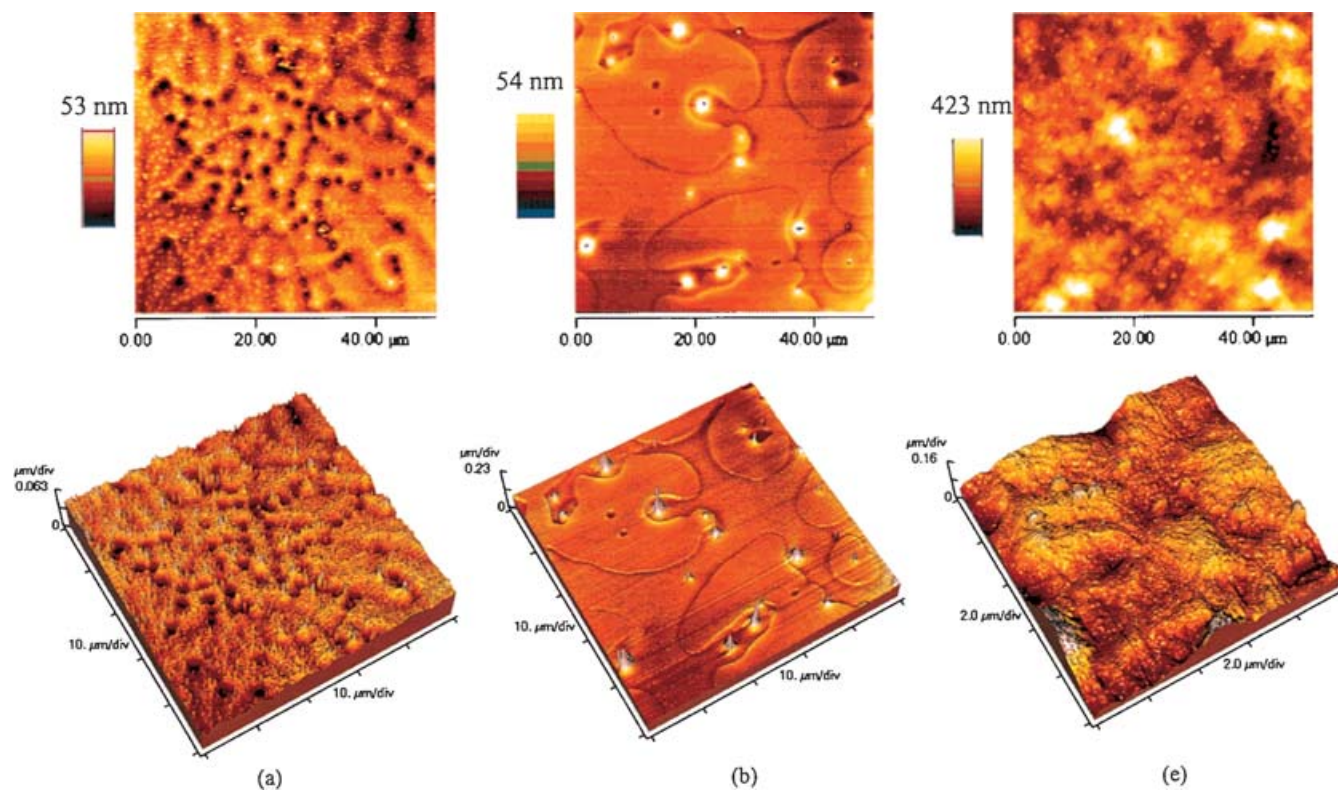


Figure 9. AFM images of the 70/15/15 ABA/BP/IA system reacted at 300°C for different times: (a) 5 min, (b) 6 min and (c) 60 min.

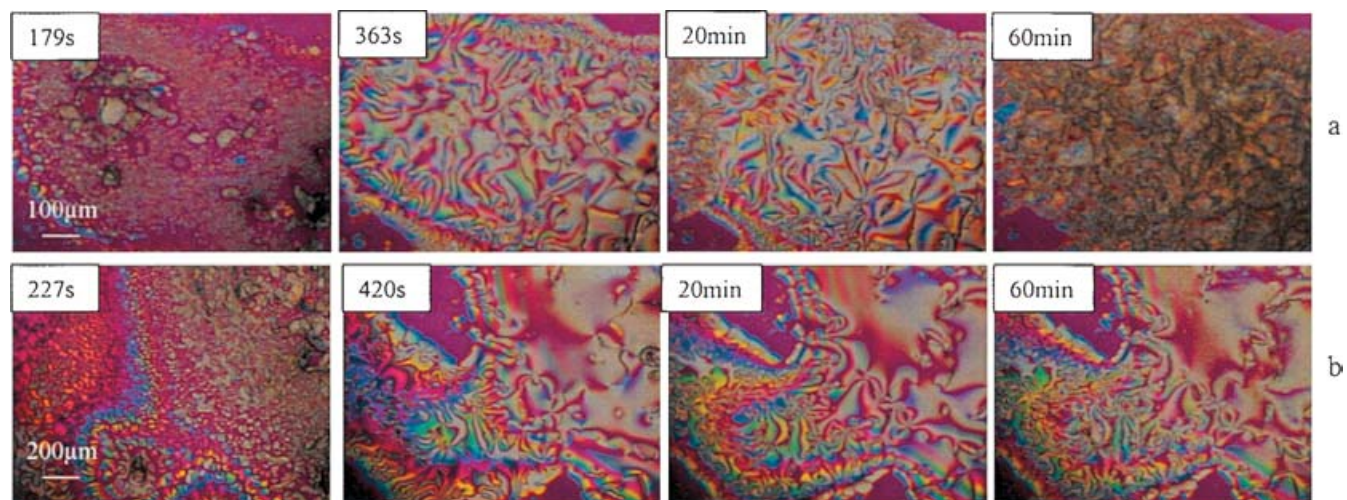


Figure 11. Micrographs showing the morphological changes of (a) 70/15/15 ABA/DABP/IA and (b) 70/15/15 ABA/BP/IA systems reacted at 380°C for 1 hr.

Table. Roughness (rms) of 70/15/15 ABA/BP/IA thin film copolymer as determined by AFM.

Reaction time/min	Roughness (rms)
5	9.14
6	10.33
8	11.03
15	29.31
30	30.62
60	87.88

At 5 min reaction time, figure 9(a), the oligomers formed are randomly distributed and undergoing formation and coalescence of nematic droplets when melting. As the pre-polymer chains are very short, the surface roughness is quite small. When the reaction time reaches 6 min, as shown in figure 9(b), a clear LC pattern has formed. A needle-shaped texture appears simultaneously; these needles have been observed to vary in height within the 40–250 nm range and in diameter within the 1.5–5 μm range. Distances between needles are generally 4–15 μm . Then coarsening, crystallization, and solidification occurs, as shown in figure 9(c). At this stage, sometimes a band-like texture could be observed for some of the compositions at certain temperature.

According to Gould and coworkers [28, 29], with soft surfaces such as PET films, the probing tip can generate irreversible indentation of the surface, thus modifying the sample surface topography [30]. We observed a similar phenomenon, and other images such as a line feature (not shown) which aligned in almost the same direction and accompanied the needle-shaped feature. However, the needle-shaped feature always appeared when the probing tip, imaging force or scan mode were changed, while the line feature disappeared with decreasing imaging force. Thus, we consider the needle-shaped feature to be true. The formation of the needle-shaped texture may be due to the vertical development of polymer chains

during thin film polymerization. This ultimately leads to an increasing R_q value as the polymerization progresses.

3.5. XRD characterization

In general the XRD patterns of nematic liquid crystals exhibit amorphous haloes, similar to those of a liquid, while the intensity at the principal maximum is 5–15% greater for nematic structure than for liquid structure. The greater sharpness of the peak, and the sharper inner slope with nematic structure, show greater regularity of structure in that phase [31]. According to de Broglie and Friedel [32, 33], molecules in the smectic structure are in equidistant parallel strata, so the sharp, high angle diffraction peaks, if any, are generally attributed to those of smectic liquid crystals. Figure 10(a) displays the wide angle XRD pattern of the thin film polymerization product of the ABA/BP/IA 70/15/15 system reacted at 380°C for 60 min on a silicon substrate. After heating the reaction mixture to 380°C and holding for 60 min, it was cooled to room temperature and the thin film thus obtained was used as the sample. No obvious morphological change was observed from POM before and after the reaction mixture was cooled to room temperature. For comparison, the XRD diffraction pattern of the blank silicon substrate was also measured and included, figure 10(b). The XRD pattern, figure 10(c), of the thin film copolymer reacted on a glass substrate also displayed a broad peak centered at about $2\theta = 25^\circ$, but was complicated by the background (substrate) diffraction pattern, figure 10(d). The XRD patterns in figure 10 suggest that a nematic liquid crystalline texture is formed for the reaction mixture after thin film polymerization.

3.6. The unit content of the polymer

As mentioned above, two different reaction mechanisms are involved in the polymerization process for the ABA/BP/IA system: one is transesterification between carboxyl groups and acetyl; the other is polycondensation

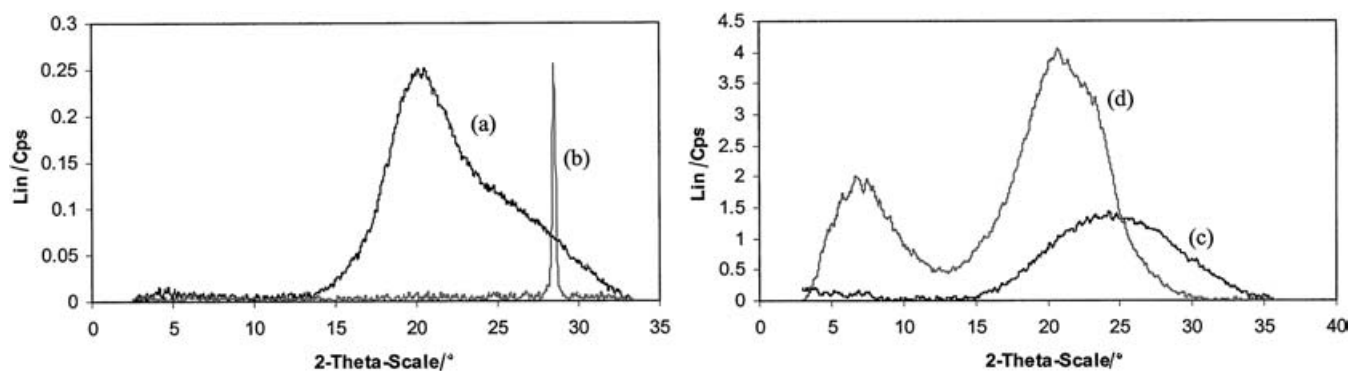
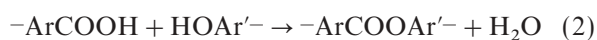
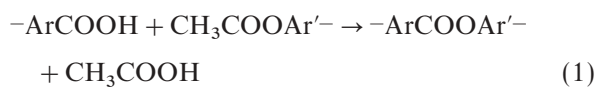


Figure 10. XRD curves for (a) the thin film copolymer 70/15/15 ABA/BP/IA reacted at 380°C for 60 min on a silicon substrate, (b) a blank silicon substrate, (c) the same system reacted at 380°C for 60 min on a glass substrate and (d) a blank glass substrate.

between carboxyl groups and hydroxy groups, as shown in equations (1) and (2), respectively (Ar and Ar' denote aromatic units).



For the ABA/BP/IA system, the reaction between ABA and IA, and between ABA and ABA eliminates acetic acid following equation (1). On the other hand, BP and IA, and BP and ABA react with elimination of water following equation (2). Although both kinds of reaction lead to the formation of aromatic ester groups, it is commonly known that the former reaction proceeds much easier than the latter [34]. This causes a doubt as to whether the reaction between BP and IA, and between BP and ABA took place and therefore, whether the BP unit was really included in the polymer backbone during the thin film polymerization process. Although FTIR spectra (figure 8) of the thin film products obtained at different reaction times suggest the absence of 4,4'-biphenol hydroxy groups in the final reaction mixture, there is no direct evidence for the existence of the BP unit in the polymer backbone.

In order to confirm that the BP unit is included in the thin film polymers formed, we employed acetylated BP, i.e. 4,4'-diacetoxybiphenyl (DABP) to replace BP in the reaction mixture. In this case, as all the hydroxy groups are acetylated, the reaction mechanism should only follow equation (1); the reactions between DABP and IA and between DABP and ABA are expected to proceed more readily than those between BP and IA and between BP and ABA. The FTIR spectrum of the thin film copolymer from the ABA/DABP/IA 70/15/15 system is shown in figure 8(e), in comparison with that of the monomer mixture, figure 8(f). It can be seen that the spectrum is actually the same as that illustrated in figure 8(d), the spectrum of the reaction product from the ABA/BP/IA 70/15/15 system. The LC texture of the ABA/DABP/IA 70/15/15 reaction system is also very similar to that of the ABA/BP/IA 70/15/15 system, as shown in figures 11(a) and 11(b), respectively. We also found from figure 11 that replacing BP with DABP did make polymerization much easier, as expected. For the ABA/DABP/IA 70/15/15 and ABA/BP/IA 70/15/15 systems processed at the same temperature of 380°C for 60 min, LC texture appeared earlier in the former than in the latter; solidification of the former started at about 20 min and was complete at about 60 min, but the latter did not begin to solidify even after 60 min reaction time.

We also carried out the thin film polymerization reaction for one- and two-monomer component systems using ABA, BP and IA as the monomers. While ABA

itself (one monomer system) polymerized easily to form a beautiful schlieren texture at low temperatures, as reported previously [22], the reaction mixtures of all the two-monomer systems, ABA/IA, ABA/BP as well as BP/IA, were found not to form LC textures. Thus if the BP component in the monomer mixture of the three-monomer system ABA/BP/IA did not take part in the polymerization process, no LC texture should have been observed. All the experimental results given above imply that the BP unit was included in the polymer obtained by the thin film polymerization method.

4. Conclusions

A LCP system based on the commercial Sumikasuper[®] LCPs was studied using the thin film polymerization approach. It was found that there existed a composition range for LC formation in the ABA/BP/IA system. Higher reaction temperature and higher ABA content are both favourable for formation of the LC phase. For each composition, there exists a critical temperature which decreases with increasing ABA content in the ABA/BP/IA system. Results from FTIR spectra of the thin film polymerization products confirm the formation of polymers. AFM investigation of the thin film surfaces reveals a similar process of morphological change during thin film polymerization as observed using POM. In addition, the XRD diffraction pattern suggests that the thin film copolymer based on Sumikasuper[®] LCPs has a nematic liquid crystal texture. Replacing BP with acetylated BP facilitates the polymerization; the FTIR spectrum and LC texture of the system with acetylated BP are similar to those of the system with BP. The two-monomer systems, BA/BP, ABA/IA and BP/IA, cannot form LC phases. These results suggest that the BP unit takes part in the polymerization process and the polymer backbone contains the BP unit.

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