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Polymer 43 (2002) 7433–7441

polymer

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Effect of a fluorine lateral moiety on the liquid crystallinity of wholly aromatic polyester-amides

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Received 23 May 2002; received in revised form 8 July 2002; accepted 10 September 2002

Abstract

We have identified the effect of a fluorine lateral moiety on the liquid crystallinity of wholly aromatic polyester-amides. The evolution of liquid crystal texture for two reaction systems, *p*-acetoxybenzoic acid (ABA)/acetoxy acetanilide (AAA)/3-fluorophthalic acid (FPA) and ABA/AAA/phthalic acid (PA), were examined and compared by in situ polymerizations under a polarizing microscope with a heating-stage. The fluorine lateral moiety was found to have an adverse effect on the liquid crystallinity. The system containing FPA needs higher critical ABA content (the rigid and straight monomer) to form liquid crystallinity than the system containing PA. In addition, the LC phase emerges faster in the ABA/AAA/PA system than in the ABA/AAA/FPA system during polymerizations. Amorphous phase reappears in the later stage of thin film polymerizations for both systems if ABA content is in a particular range. However, the ABA/AAA/FPA system has a greater amorphous area than the ABA/AAA/PA system. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystalline polymer; Liquid crystallinity; Fluorine

1. Introduction

Thermotropic liquid crystalline polymers have unique combination of favorable properties and have been widely used as high value-added electronics and composite materials [1–5]. Significant research attention has been given to investigate the relationships among the monomer structures, synthesis conditions and end-use properties of liquid crystalline polymers (LCPs) [1,3–9]. Most monomers for LCP synthesis do not possess characteristics of liquid crystallinity. During the polymerization, the liquid crystal (LC) phase forms, and the LC texture evolves with the progress of the polymerization. Although there is a fair amount of knowledge about structures of liquid crystalline phases, it is still not very clear what causes liquid crystallinity exactly. Using a thin film polymerization technique, our research group has conducted various LCP polymerizations and examined their in situ morphological changes to study the reaction kinetics and the effects of kinks on the liquid crystallinity [10–14]. We found that the formation of liquid crystallinity was determined not only by the aspect ratio and rigidity of monomers, but also by their conformation and the polymerization temperature. For example, the copolymerization systems of ABA/AAA/isophthalic acid (IA) and 2,6-acetoxynaphthoic acid (ANA)/AAA/IA have critical content of the rigid monomer, ABA or ANA, to form the liquid crystalline phase. Below this critical content, crystals form during polymerization [12]. In comparison of ANA/AAA/IA and ANA/AAA/PA systems, the *ortho* linkage in the PA unit was found to have a higher tendency to yield liquid crystallinity than the *meta* linkage in the IA unit [14]. In this paper, we intend to apply this thin film polymerization technique to investigate the effect of a lateral group on the liquid crystallinity. To our knowledge, the exact role of lateral groups has not been well studied.

To identify the exact effect of a lateral group on the formation of liquid crystallinity, two reaction systems, ABA/AAA/FPA and ABA/AAA/PA, were chosen to carry out our study and their polymerizations under a polarizing microscope with a heating-stage were compared in detail.

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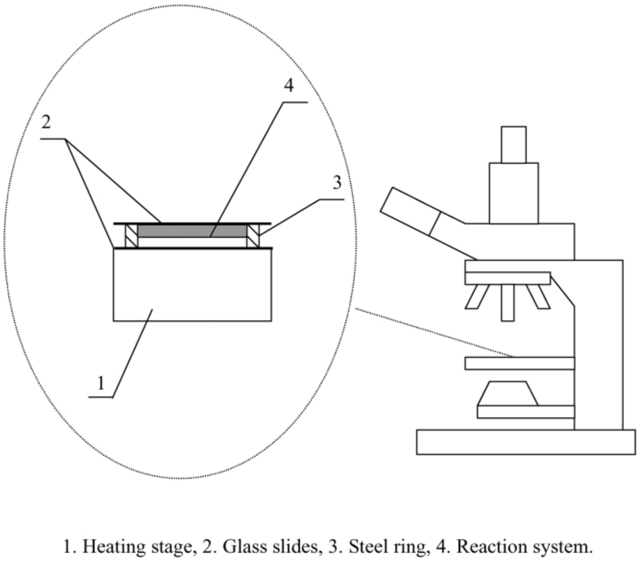
PII: S0032-3861(02)00679-1



1. Heating stage, 2. Glass slides, 3. Steel ring, 4. Reaction system.

Fig. 1. The sample for thin film polymerization.

2. Experimental

2.1. Preparation of monomers

p-Acetoxybenzoic acid (ABA) was made by the acetylation of *p*-hydroxybenzoic acid (HBA), with acetic anhydride in refluxing toluene in the presence of a catalytic amount of pyridine. The prepared monomer was then purified by recrystallization in methanol. Acetoxy acetanilide (AAA) was obtained by acetylation of *p*-aminophenol with acetic anhydride in the NaOH solution at a low temperature. The as-prepared AAA was then recrystallized from methanol/hexanes. 3-Fluorophthalic acid (FPA) and phthalic acid (PA) were purchased from Aldrich and utilized as received.

The melting points of ABA, AAA, FPA and PA measured by DSC (Perkin Elmer DSC Pyris 1) are 196, 157, 176 and 205 °C, respectively.

2.2. Thin film polymerization

Monomer mixture with certain mole ratio was placed on a glass slide. A drop of acetone was deposited on the glass slide to dissolve monomers. After evaporation of the solvent, a thin layer of reactant mixture was formed and attached to the glass slide, and then sandwiched between two glass slides with a ring spacer. The monomers were attached on the top slide. The ring spacer was made of stainless steel with a thickness of 0.5 mm. The whole package was placed on a heating stage (Linkam THMS-600) of a microscope and heated to the proposed temperature. The sample was held at that specific temperature during the whole reaction process. When the heating stage reached the proposed temperature, the reaction time began to be recorded. The temperature of the top slide was calibrated by testing the melting points of the pure monomers as well as by measuring with a thermocouple. The temperature difference between the heating stage set by the programmer and the top slide was 20 ± 2 °C in the experimental temperature range. The polymerization reaction was carried out on the top slide and all the temperatures mentioned refer to the temperatures of the top slide. The reaction process was observed in situ by a polarizing light microscope (Olympus BX50) with crossed polarizers between which a red plate having the retardation of 530 nm was inserted or not inserted. The optical images were recorded and analyzed by a commercial software (Image-Pro Plus 3.0). The sample for the thin film polymerization is shown in Fig. 1.

2.3. Characterizations

2.3.1. Fourier transform infrared spectroscopy (FTIR)

The monomer mixtures and polymers were characterized by FTIR (Perkin Elmer FTIR Spectrometer Spectrum 2000). Polymer samples (in KBr pellets) were prepared by scraping the polymerization products from the glass slides.

2.3.2. Dielectric analysis (DEA)

Some fluorine-containing thin film polymerization products were characterized by DEA (TA Dielectric Analyzer 2970).

3. Results and discussion

3.1. Characters of monomer structure

The monomers selected for this study are shown in Fig. 2. As we know, chain straightness plays an important role to form liquid crystallinity. *p*-Acetoxybenzoic acid (ABA) provides a benzene ring which potentially to be a mesogenic unit, and forms an ester unit during polymerization. Since the ester groups consist of angular bridging groups with parallel conformation and keep the 1,4-axes of the benzene rings to lie parallel, the ester linkage provides little opportunity for a chain to kink, and keeps the chain straight [1]. Similarly, acetoxy acetanilide (AAA) provides a benzene ring potentially acting as a mesogenic unit, an amide group and an ester group as bridging groups to keep the chain conformation straight.

Phthalic acid (PA) is a monomer with an *ortho* linkage that can introduce a kink into the molecular chain, which disturbs the chain straightness and packaging of the resultant polymers. This monomer may be used to lower the transition temperatures of LCPs. However, the *ortho* linkage has a detrimental effect on the stability of the LC phase because it disturbs the characteristics of liquid crystallinity if its percentage is too high [1,12]. The chemical structure of 3-fluorophthalic acid (FPA) is quite similar to that of PA as drawn by the Chem-3D Pro software and shown in Fig. 3. The only difference between them is a fluorine atom replaces the hydrogen atom on the

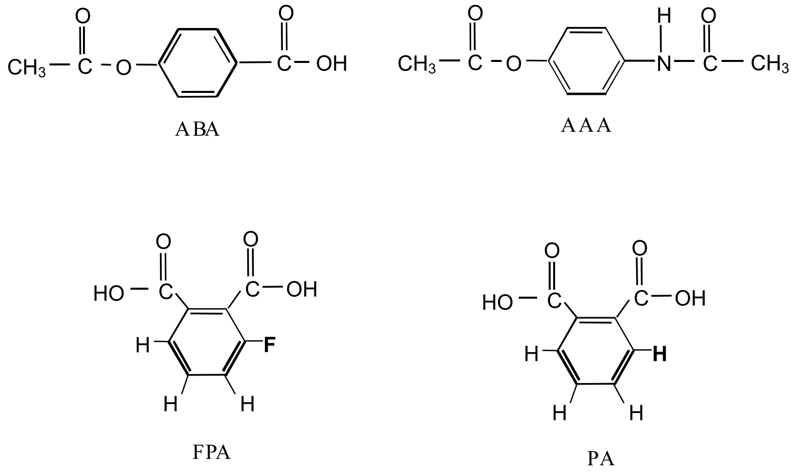


Fig. 2. Chemical formulas of the monomers.

benzene ring. Because of the kink structure in FPA and PA units, the two reaction systems we studied, ABA/AAA/FPA and ABA/AAA/PA, have the critical content to form liquid crystallinity. In addition, the different sizes of fluorine and hydrogen atoms also affect the formation of liquid crystallinity. We selected FPA as the lateral fluorine (F) substituted monomer because the covalent radius of F atom is 0.72 Å, which is quite closed to that of H atom with a covalent radius of 0.32 Å [Periodic Table of the Elements]. The minor difference between these two systems gives us the provision to identify the exact role of the lateral fluorine substituted group and its contribution to the formation of liquid crystallinity during thin film polymerization.

3.2. Comparison of the thin film polymerizations of ABA/AAA/FPA system and ABA/AAA/PA system

Based on the observation of a polarizing microscope, the critical ABA content to form the LC phase for ABA/AAA/FPA and ABA/AAA/PA systems was found to be 9 and 5 mol%, respectively, at 280 °C. If the ABA content is lower than the corresponding critical value, only amorphous products are observed during the entire process of polymerizations, while LC phase appears during the reaction if the ABA content is higher than the corresponding critical value.

In the following sections, a detailed comparison is made for these two reaction systems with different ABA content ranging from 80 to 14 mol%. Figs. 4 and 5 show the generation of LC phase and the evolution of LC texture for the reaction systems of ABA/AAA/FPA and ABA/AAA/PA containing 80% ABA at 280 °C. As shown in Fig. 4, the copolymerization system of 80/10/10 ABA/AAA/FPA starts from a homogenous phase and then changes into a heterogeneous system. When the sample is heated to the proposed reaction temperature, monomers melt and the whole view area becomes an isotropic melt phase (90 s). In the early stage of polycondensation reaction, oligomers are formed in the molten monomer phase. Their molecular weights and chain lengths increase with reaction time. When their chain lengths reach a certain value, the

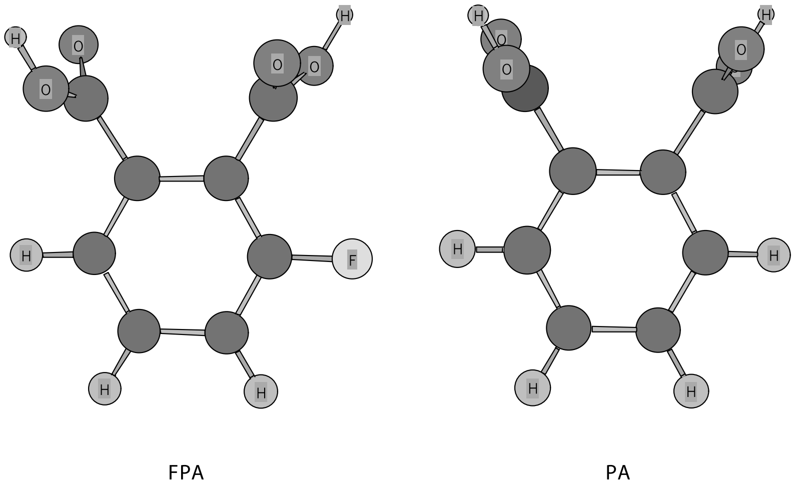


Fig. 3. Comparison of the molecular structures of FPA and PA.

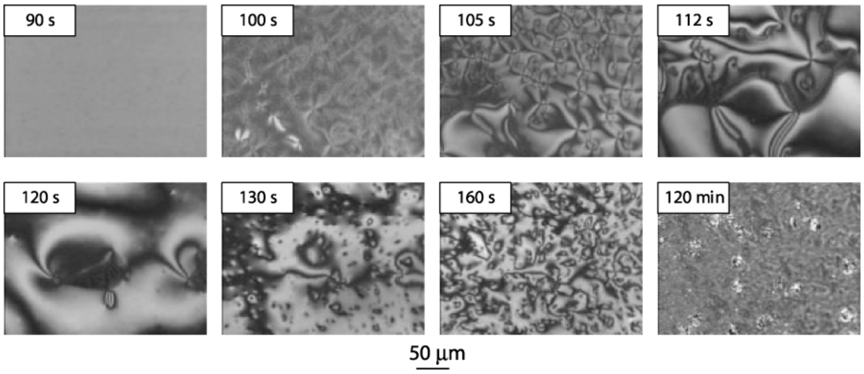


Fig. 4. Micrographs showing morphologies of 80/10/10 ABA/AAA/FPA polymerization reaction system at different reaction times. All the micrographs were obtained from the same area of the same sample. Reaction temperature: 280 °C.

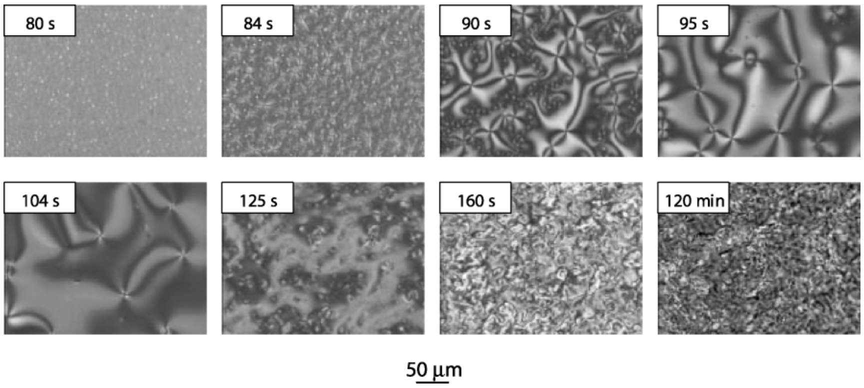


Fig. 5. Micrographs showing morphologies of 80/10/10 ABA/AAA/PA polymerization reaction system at different reaction times. All the micrographs were obtained from the same area of the same sample. Reaction temperature: 280 °C.

oligomers form an LC phase and separate from the isotropic melt. As shown in Fig. 4 (100 s), the dark area in the micrograph is the isotropic phase, while the bright area represents the LC phase. Because of the polydispersity of the chain length, oligomers are partitioned within the isotropic and the LC phases according to the chain length as well as the monomeric unit distribution. After the formation of LC domains, the annihilation between disclinations occurs to reduce free energy. This annihilation process was discussed in detail in our pervious papers [10,11]. The LC phase increases quickly within a very short period of time. When the reaction time is 112 s, the total view area becomes the LC phase. After 130 s, crystallization begins to occur. For the polymerization of 80/10/10 ABA/AAA/PA, Fig. 5 depicts similar morphological changes to that of 80/10/10 ABA/AAA/FPA. The annihilation in these two systems needs about 30 s. The common phenomenon for the 80/10/10 ABA/AAA/FPA and the 80/10/10 ABA/AAA/PA systems is crystallization, which is caused by the high ABA content, occurring after LC phase forms in the whole view area.

The morphologies of 60/20/20 ABA/AAA/FPA and

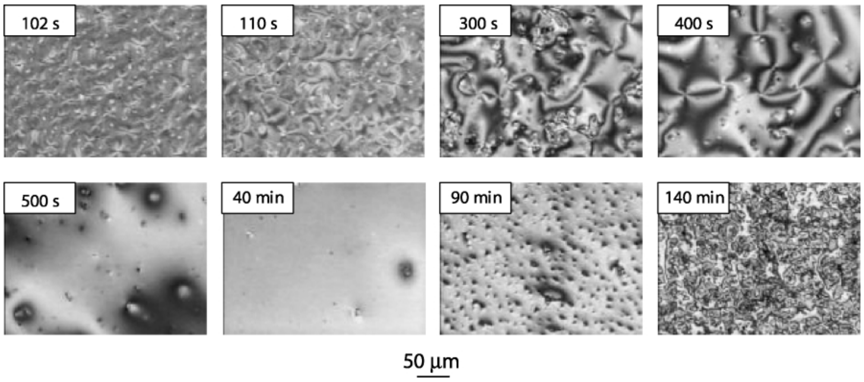


Fig. 6. Micrographs showing morphologies of 60/20/20 ABA/AAA/FPA polymerization reaction system at different reaction times. All the micrographs were obtained from the same area of the same sample. Reaction temperature: 280 °C.

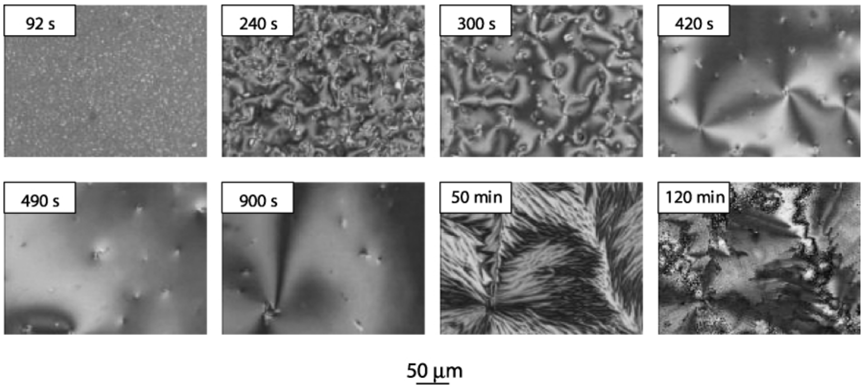


Fig. 7. Micrographs showing morphologies of 60/20/20 ABA/AAA/PA polymerization reaction system at different reaction times. All the micrographs were obtained from the same area of the same sample. Reaction temperature: 280 °C.

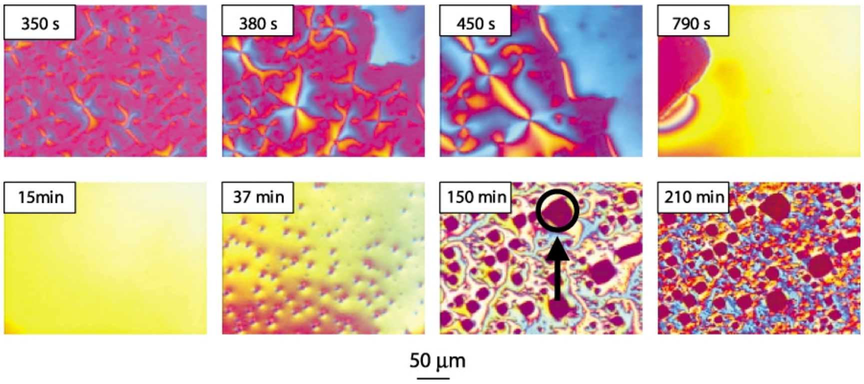


Fig. 8. Micrographs showing morphologies of 40/30/30 ABA/AAA/FPA polymerization reaction system at different reaction times. All the micrographs were obtained from the same area of the same sample. Reaction temperature: 280 °C.

60/20/20 ABA/AAA/PA systems are shown in Figs. 6 and 7, respectively. Compared to the 80/10/10 ABA/AAA/FPA and the 80/10/10 ABA/AAA/PA systems, the current systems have much slower annihilation processes during the early stage of reactions, both take more than 200 s to annihilate completely. Clearly, the lower the ABA content, the slower the annihilation. This phenomenon is caused by the lower elastic constant values for the system having a lower concentration of ABA. Because the persistence length decreases with decreasing ABA content and thus the elastic constants decrease [11,15–17], the annihilation in the lower ABA containing system is slower.

By further decreasing ABA content, interestingly, we found the reappearance of amorphous phase in the late stage of reactions for both 40/30/30 ABA/AAA/FPA (Fig. 8) and 40/30/30 ABA/AAA/PA (Fig. 9) systems. The circles in the figures highlight typical examples. The color of these domains does not change when we rotate the crossed polarizers, indicating the domains are in isotropic state. The domain area increases with increasing reaction

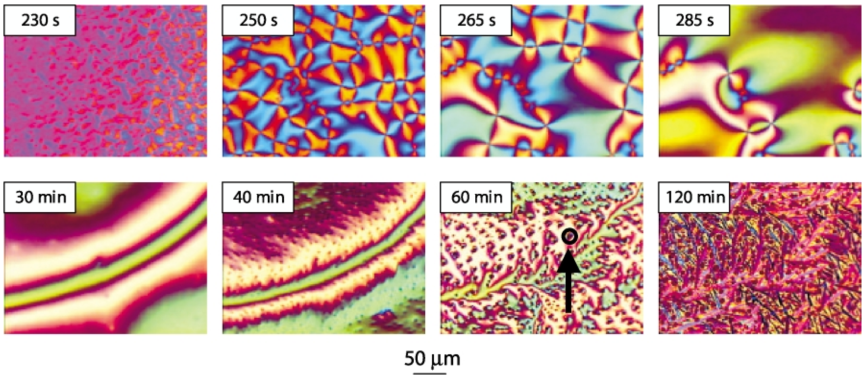


Fig. 9. Micrographs showing morphologies of 40/30/30 ABA/AAA/PA polymerization reaction system at different reaction times. All the micrographs were obtained from the same area of the same sample. Reaction temperature: 280 °C.

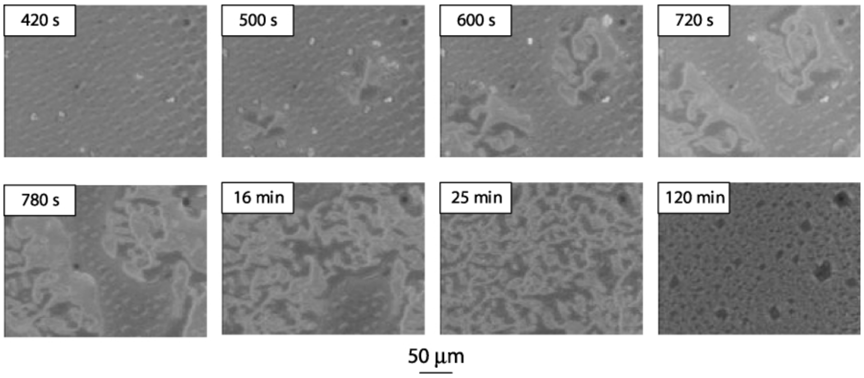


Fig. 10. Micrographs showing morphologies of 20/40/40 ABA/AAA/FPA polymerization reaction system at different reaction times. All the micrographs were obtained from the same area of the same sample. Reaction temperature: 280 °C.

time. As reported by other researchers, transesterification reactions occur during the late stage of polymerization [18, 19]. From our interesting phenomenon, we believe it is caused by a slight change in persistence length because of the rearrangement of monomeric units induced by the transesterification. As the persistence length in these systems is very close to the critical persistence length to form liquid crystallinity and the monomeric units are not totally randomly distributed in the polymeric chains [20], transesterification causes the persistence lengths in some areas to be lower than the critical value, as a result the LC phase changes to the isotropic phase. Comparing these two systems, one can find the amorphous area in the system containing FPA is obviously larger than that in the system containing PA, which suggests the adverse effect of large F atom on the liquid crystallinity.

As we expected, the LC areas become smaller and the appearance of LC phases is delayed if we further decrease ABA content in the two systems. Figs. 10 and 11 show the morphology evolutions during the thin film polymerizations for 20/40/40 ABA/AAA/FPA and 20/40/40 ABA/AAA/PA systems, respectively. In the 20/40/40 ABA/AAA/FPA system, the bright LC domains appear when reaction time is around 420 s. The LC droplets coalesce and later form interconnect domains. In the late stage of the reaction, the LC texture becomes unclear. For the 20/40/40 ABA/AAA/PA system, the point we want to emphasize is also the reappearance of the isotropic phase in the late reaction stage. Different from the 20/40/40 ABA/AAA/FPA system where the LC texture becomes unclear, the character of this system is that the formation and increase of amorphous phase after the reaction time reaches 15 min. Although the morphology of the final product looks quite like crystals, it is actually a structure consisting of the LC phase and amorphous phase as can be clearly seen in Fig. 11 (15–120 min), which monitors the appearance process of the amorphous phase.

For 14/43/43 ABA/AAA/FPA system (Fig. 12), the LC phase emerges when reaction time is 510 s. The LC areas increase slowly with the progress of reaction, and reach the maximum when reaction time reaches 540 s. At this moment, the LC phase still exists as separate LC droplets, and the droplets are dispersed in the amorphous phase. Afterwards the LC texture becomes coarse and unclear with further increasing reaction time. For 14/43/43 ABA/AAA/PA system (Fig. 13), it takes a shorter time (370 s) to generate the LC phase. The LC droplets then increase and coalesce with each other. The LC phase covers most of the view area when reaction time reaches 540 s, however the amorphous phase still exists in the system. Similar to the system containing FPA, the LC texture also becomes unclear during the late stage of polymerization. In these two

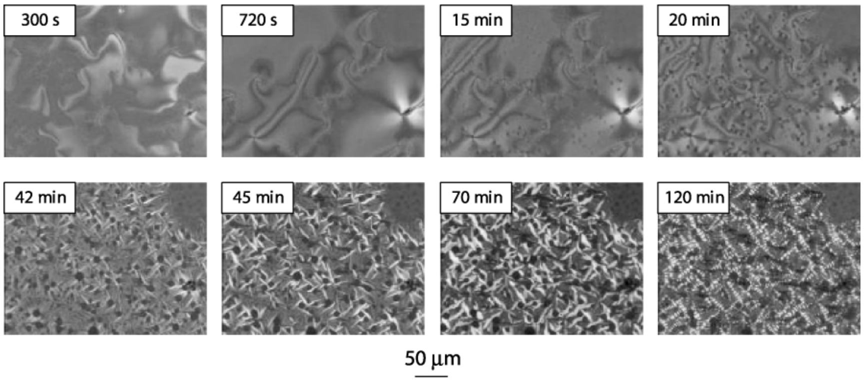


Fig. 11. Micrographs showing morphologies of 20/40/40 ABA/AAA/PA polymerization reaction system at different reaction times. All the micrographs were obtained from the same area of the same sample. Reaction temperature: 280 °C.

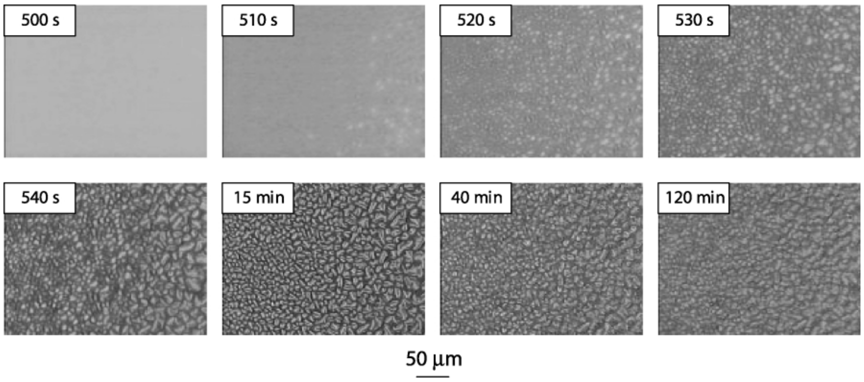


Fig. 12. Micrographs showing morphologies of 14/43/43 ABA/AAA/FPA polymerization reaction system at different reaction times. All the micrographs were obtained from the same area of the same sample. Reaction temperature: 280 °C.

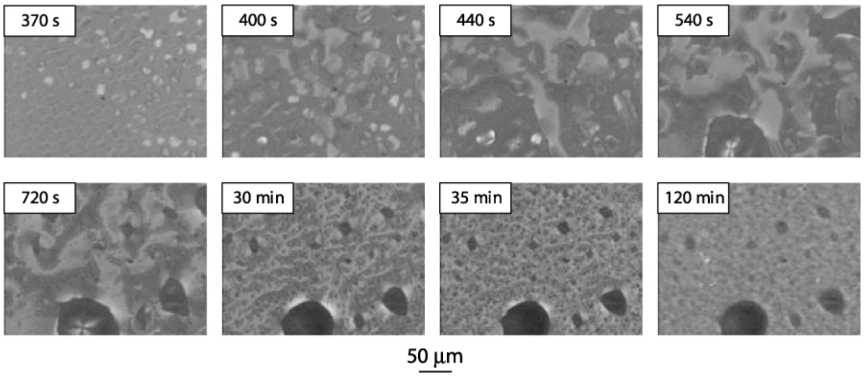


Fig. 13. Micrographs showing morphologies of 14/43/43 ABA/AAA/PA polymerization reaction system at different reaction times. All the micrographs were obtained from the same area of the same sample. Reaction temperature: 280 °C.

reaction systems, the coexistence of LC phase and amorphous phase is because the persistence ratio in these systems is very close to the critical persistence ratio to form liquid crystallinity, which is due to the fact that the two systems have the high kink contents (FPA or PA). Fig. 12 indicates that the LC droplets in the system containing FPA are difficult to coalesce. This may arise from the following two reasons. First, the system containing F element has lower surface energy so that the LC droplets are trend to exist separately. Second, since the ABA/AAA/PA system has a greater tendency to form liquid crystallinity than the ABA/AAA/FPA system, the former has a bigger LC area than the latter. Thus, the LC droplets in the ABA/AAA/PA system have a higher chance to coalesce than in the ABA/AAA/FPA system.

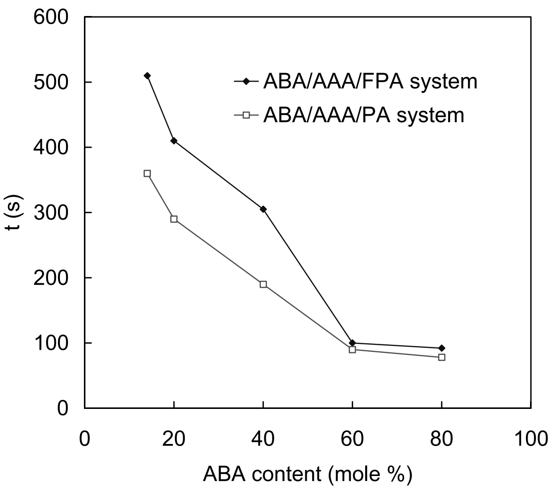


Fig. 14. The dependence of LC phase generation time on monomer ABA content. Reaction temperature: 280 °C.

From the thin film polymerization results mentioned earlier, we can deduce that the fluorine lateral moiety has an unfavorable effect on the liquid crystallinity. The LC phase generation time for the two polymerization systems, ABA/AAA/FPA and ABA/AAA/PA, is summarized in Fig. 14. For each particular ABA content, the ABA/AAA/FPA system needs longer time to generate LC phase than the ABA/AAA/PA system, especially when the kinked monomer, FPA or PA, content is high in the copolymerization system. Although the structures of FPA and PA seem similar, the fluorine atom in FPA has a larger size, which indeed reduces the liquid crystallinity for the system containing FPA because the larger size results in a lower persistence ratio of the resultant copolymer. It is well known that the introduction of lateral groups into polymer backbones can dramatically decrease the transition temperatures of resulting LCPs. However, the bulky lateral groups also greatly reduce the liquid crystallinity so that it is

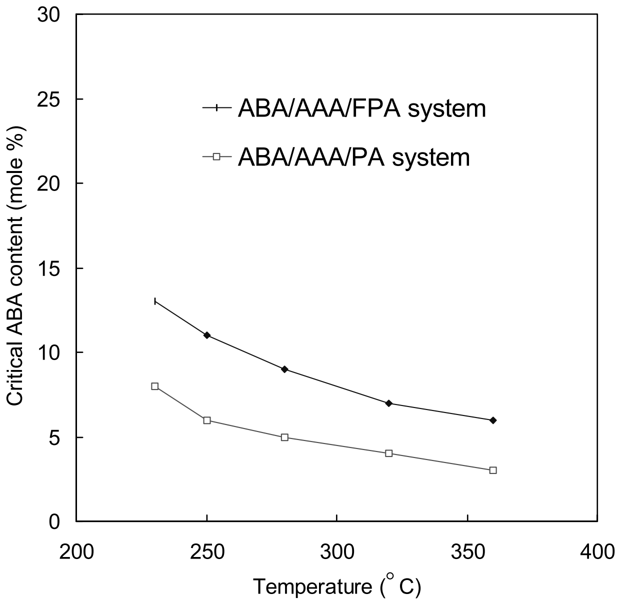


Fig. 15. The critical ABA content to form liquid crystallinity at different reaction temperatures.

important to control the content of the monomeric units with bulky lateral groups [3]. It is also reported that the size difference between the fluorine atom and the hydrogen atom can affect the crystal structures of many compounds [21]. Therefore, it is not strange that the small structure difference between FPA and PA monomers causes obvious differences in the formation of liquid crystallinity. The critical ABA content to form liquid crystallinity is another important criterion showing the influence of the fluorine lateral moiety. As shown in Fig. 15, the critical ABA content to generate the LC phase during the polymerization of ABA/AAA/FPA system is higher than ABA/AAA/PA system, which implies that the system containing PA has a greater tendency to form the liquid crystallinity.

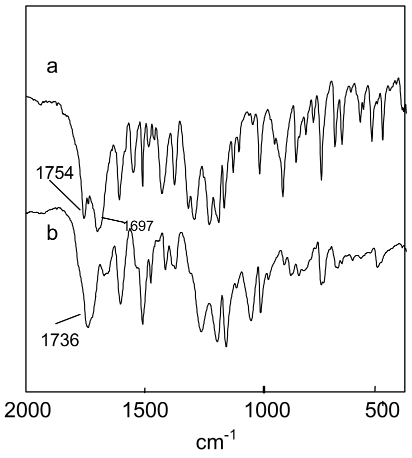


Fig. 16. FTIR spectra of monomers and the thin film polymerization product for 60/20/20 ABA/AAA/FPA reaction system. (a) Monomers and (b) product of 2 h reaction at 280 °C.

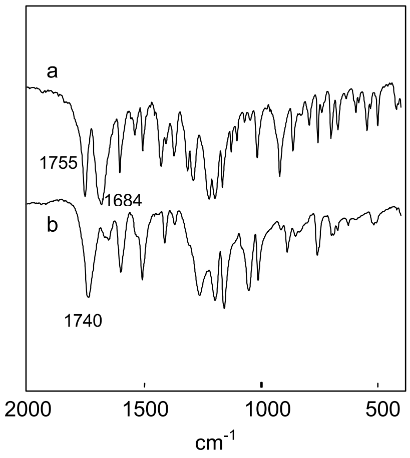


Fig. 17. FTIR spectra of monomers and the thin film polymerization product for 60/20/20 ABA/AAA/PA reaction system. (a) Monomers and (b) product of 2 h reaction at 280 °C.

3.3. FTIR characterization

Figs. 16 and 17 are the FTIR spectra for monomers and thin film products of 60/20/20 ABA/AAA/FPA and 60/20/20 ABA/AAA/PA systems, respectively. For the ABA/AAA/FPA system, the band at 1697 cm^{-1} is for $\nu_{\mathrm{C=O}}$ of –COOH and 1754 cm^{-1} is for $\nu_{\mathrm{C=O}}$ of CH_3COO– of monomers. These bands almost completely disappear after reaction. The band of ester groups formed at 1736 cm^{-1} indicates the formation of a polymer. We observed similar changes in the spectra of the monomer mixture and the polymer for 60/20/20 ABA/AAA/PA system, showing the formation of a copolymer.

3.4. DEA characterization

The fluorine-containing polymers usually have low permittivity, which makes them having wide applications in electronics. In the research of novel LCPs, substituting the H atom in the aromatic backbone with the F atom has been proven to be an effective way to decrease the transition temperature [22]. Figs. 18 and 19 show the permittivity vs.

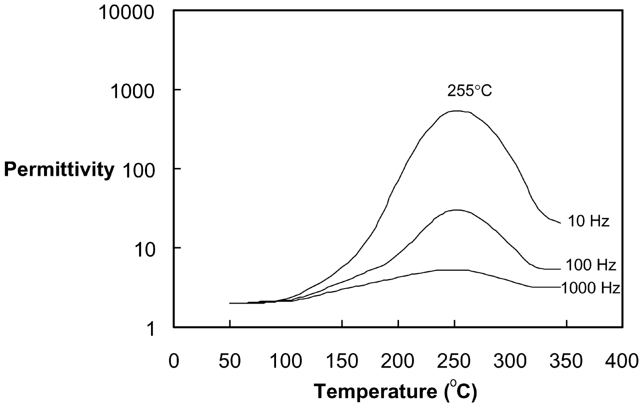


Fig. 18. The dielectric property of 40/30/30 ABA/AAA/FPA thin film polymerization product.

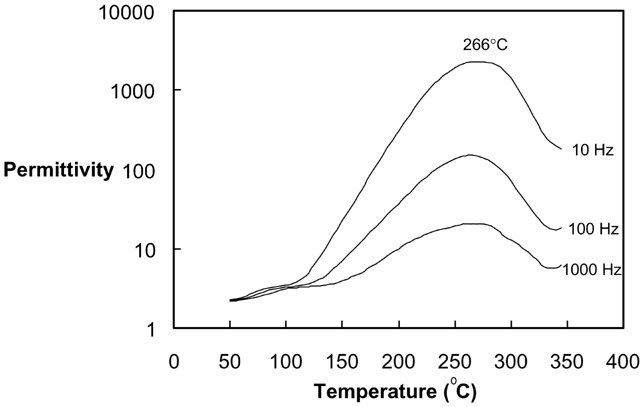


Fig. 19. The dielectric property of 60/20/20 ABA/AAA/FPA thin film polymerization product.

temperature at different frequencies for the thin film polymerization products with the compositions of 40/30/30 ABA/AAA/FPA and 60/20/20 ABA/AAA/FPA, respectively. The DEA experimental results are in good agreement with the pervious study [22]. From the two series of permittivity curves, it can be found that the high fluorine-containing product (30% FPA) has a lower transition temperature (255 °C at 10 Hz) than that (266 °C at 10 Hz) of the low fluorine-containing product (20% FPA). Also the former has a lower permittivity value than the latter.

4. Conclusions

Through the in situ thin film polymerization under a polarizing microscope, the effect of a fluorine lateral moiety on liquid crystallinity has been determined by comparing two reaction systems, *p*-acetoxybenzoic acid (ABA)/acetoxy acetanilide (AAA)/3-fluorophthalic acid (FPA) and ABA/AAA/phthalic acid (PA). Because of the kink structure of PA and FPA units, these polymerization systems have critical compositions to form liquid crystallinity. The system containing FPA needs higher critical ABA content to form liquid crystallinity than the system containing PA. In addition, the different sizes of fluorine and hydrogen atoms obviously affect the formation of liquid crystallinity and morphology of reaction systems. In the early stage of reaction, the LC phase emerges earlier for the ABA/AAA/PA system than for the ABA/AAA/FPA system. Amorphous phases reappear in the later stage of thin film polymerizations for both systems if ABA content is in a particular range. However, the ABA/AAA/FPA system has a greater amorphous area than the ABA/AAA/PA system, indicating the unfavorable effect of the fluorine lateral moiety on liquid crystallinity.

Acknowledgements

The authors would like to express their gratitude to National University of Singapore (NUS) for the research fund RP3982739. Thanks are also due to the Institute of Materials Research and Engineering (IMRE) for using the equipment. Special thanks are to Dr S. Mullick for providing the monomers, Dr C.B. He and Mdm L.K. Leong for their kind help.

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