Effect of $-C(CF_3)_2$ on the Surface Energy of Main-Chain Liquid Crystalline and Crystalline Polymers

Kui-Xiang Ma and Tai-Shung Chung*

Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, and Department of Chemical & Environmental Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

Received: August 28, 2000; In Final Form: December 12, 2000

Novel fluorinated main-chain liquid crystalline/crystalline polymers were prepared through thin film polymerization. Two polymer systems were studied: one from 2,6-acetoxynaphthoic acid (ANA), acetoxy-acetanilide (AAA), and 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (6F acid) and the other from ANA, hydroquinone diacetate (HQAT), and 6F acid. The surface energy was estimated using contact angles of water, glycerol, and diiodomethane. A small amount of $-C(CF_3)_2$ - in the main chain lowered the surface energy and the fluorocarbons were preferentially enriched at the air-polymer interface, causing low surface energy and large water contact angles. These results agreed with XPS data. Since the -O-Ar-O- unit in the HQAT moiety is more rigid than the -O-Ar-N- unit in the AAA moiety, LC texture formed more easily in the ANA/HQAT/6F acid system than in the ANA/AAA/6F acid system. Contrarily, the fluorocarbons enriched more preferentially at the surface in the ANA/AAA/6F acid system than in the ANA/HQAT/6F acid system. Moreover, the hydrogen bonding originating from the amide group hindered further decrease of surface energy with an increase in 6F acid content in the ANA/AAA/6F acid system.

1. Introduction

Fluorine's small size, large electronegativity, low polarizability, and large fluorine-fluorine repulsion lead to many interesting properties of fluoro polymers.¹ The low intermolecular forces present in fluorinated polymers have been recognized to account for the relatively low surface energy. As a result, fluorine-containing polymers are generally difficult to wet with liquids; moreover, these surfaces tend to have nonadhesive character and low coefficients of friction.² Due to the unique nonwetting property, fluorinated polymers have been used for imparting oil- and water-resistance applications.³

It has been reported and accepted that the low surface energy of a fluoro-containing polymer is caused by segregation of the fluorinated segment to the surface, which creates a hydrophobic surface. Grinten et al.⁴ investigated a typical UV-curable resin mixed with fluorine-ended monomers through photopolymerization and observed surface segregation. The fluoro monomer was preferentially enriched at the air interface when the curable mixture was coated on a polar substrate, whereas the monomer was found to preferentially reside at both interfaces when the mixture was coated on an apolar substrate.

Chapman et al. synthesized and characterized fluorinated poly(amide urethane) block copolymers, which were fluorinated on both side chain and main chain.^{5–8} Their studies demonstrated that poly(amide urethanes) with tertiary polyamide soft blocks containing fluorinated side chains could phase-segregate giving a surface of exposed fluorocarbons, shown by the low critical surface tension. The existence of fluorine in the main chain appeared not to have significant influence on the interfacial properties if there were fluorinated side chains. Their results

demonstrated that the fluorinated side chains had a profound influence on the composition-depth profiles. The longer the fluorinated side chains, the thicker the fluorine-rich layer in the surface.

Kim et al. synthesized urethane graft copolymers with both perfluoroalkyl- and silicone-containing side chains and investigated their surface properties.^{9,10} The lowest surface energies were found to be $9-12 \text{ mJ/m}^2$, which was dependent strongly on perfluoroalkyl content but not on trimethylsilyloxy content. Together with XPS analysis, their results confirmed that perfluoroalkyl group was more preferentially enriched to the outermost layer than the silicone-containing group.

Ober et al. studied the surface properties of a series of block polymers synthesized from tetrahydropyranyl methacrylate and fluorinated methacrylates.^{11–13} They found that the length of fluorocarbon units in the side chain gave different liquid crystalline phases, which affected their critical surface tension and surface stability. The semifluorinated liquid crystal polymer with smectic B packing had the most stable surface.¹³

A thin film polymerization technique has recently been developed for LCP studies.^{14,15} This technique has some advantages over the bulk synthesis: for example, it consumes extremely small amounts of monomers, and the evolution of morphological changes and liquid crystal formation during the entire polycondensation reaction can be observed. Comparing the thin film polymer of 73/23 (mole ratio) *p*-acetoxybenzoic acid (ABA)/2,6-acetoxynaphthoic acid (ANA) to the commercial Vectra A-950 LCP (Hoechst Celanese), we found that their reaction kinetics followed the same second order and the activation energies of the polycondensation reaction for both systems were quite similar.¹⁶ In addition, the FTIR spectrum, the total surface energy, and its Lewis acid and base components of the thin film copolymer were identical to those of the

^{*} To whom correspondence should be addressed. Fax: 65-8748388. E-mail: chencts@nus.edu.sg.

commercial LCP.¹⁷ These results indicated that the polymeric film synthesized by the thin film polymerization technique is suitable for surface energy and contact angle measurements, as polymers rather than oligomers obtained after the thin film polymerization.

The purpose of the present study was to investigate the effect of $-C(CF_3)_2$ on the surface energy of main-chain liquid crystalline (LCPs) and crystalline polymers. LCPs were chosen because of their unique anisotropic mechanical properties, excellent chemical resistance, and high thermal stabilities.^{18–22} The incorporation of fluorine atoms into thermotropic LCPs may alter their physical properties for other medical applications.²³ Two series of aromatic thermotropic LCPs were prepared: one from 2,6-acetoxynaphthoic acid (ANA), acetoxyacetanilide (AAA), and 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (6F acid) and the other from ANA, hydroquinone diacetate (HQAT), and 6F acid. A thin film polymerization technique was utilized to prepare copolymers samples. The formation of liquid crystalline/crystalline was examined under a polarized microscope (PLM). Surface properties of the resulting copolymers were investigated with the aid of a contact angle goniometer and X-ray photoelectron spectroscopy (XPS).

2. Experimental Section

2.1. Monomers. Monomer ANA was prepared by acetylation of 2,6-hydroxynaphthoic acid (HNA) with acetic anhydride in refluxing toluene in the presence of pyridine, followed by recrystallization of ANA in methanol. AAA was obtained by acetylation of *p*-aminophenol with acetic anhydride in NaOH solution, followed by recrystallization in a mixture of methanol and hexane with a volume ratio of 50:50. NMR confirmed the success of acetylation. Monomers HQAT and 6F acid were purchased from Aldrich and used as received. The melting points of ANA, AAA, HQAT, and 6F acid were 226, 157, 121, and 272 °C, respectively.

2.2. Thin Film Polymerization. Monomer mixture with a certain mole ratio was placed on a microglass slide, followed by depositing several drops of acetone to dissolve monomers, to yield a thin layer of reactant mixture attached to the microglass slide after acetone evaporation. The microglass slide containing monomers was sandwiched by another glass slide and spaced about 0.5 mm by aluminum foil. The monomers were attached to the top slide. The spacer provides the channel for the removal or release of acetic acid during polymerization. The whole set was then wrapped by aluminum foil with the glass slide containing the monomer facing down and heated on a digital hot plate at 300 °C \pm 1% for 3 h. After reaction, the whole package was removed from the hot plate and cooled under ambient temperature (~ 25 °C). The resulting thin film copolymer on the top microglass slide was used for contact angle measurements.

To examine the optical morphology of the entire polycondensation reaction, the above process was also conducted in situ under a hot staged polarizing light microscope, PLM (Olympus BX50, Tokyo, Japan), and the details of experiments have been published elsewhere.¹⁴

2.3. Polymer Characterizations. The thin film copolymers with different monomer compositions were scratched from glass slides and characterized without any further treatment. Infrared measurements were conducted on a Perkin Elmer FTIR spectrometer spectrum 2000, where samples were mixed with KBr for IR spectrum. A Perkin Elmer thermogravimetric analyzer (TGA 7) was used to investigate the thermal stability of the thin film copolymers, at a scanning rate of 20 °C/min. Thermal

TABLE 1: Surface Tension Parameters (in mJ/m^2) of Testing Liquids

parameter	water	glycerol	diiodomethane
γ^+	25.5	3.92	0.0
γ^{-}	25.5	57.4	0.0
γ^{AB}	51.0	30.0	0.0
γ^{LW}	21.8	34.0	50.8
γ	72.8	64.0	50.8
γ^{p}	51.0	26.4	2.3
γ^{d}	21.8	37.0	48.5
γ	72.8	63.4	50.8

analysis was carried out with a TA Instruments differential scanning calorimetry (DSC) 2920. For DSC, samples were heated from 50 to 390 °C at a rate of 10 °C/min. For modulated DSC (MDSC), samples were heated from 50 to 390 °C at a rate of 2 °C/min and modulated at \pm 1 °C every 30 s. All the experiments were run under nitrogen atmosphere. Inherent viscosity (IV) of the thin film copolymers was tested by capillary rheometer in 3,5-bis(trifluoromethyl)phenol (BTMP) solution (0.1 g/dL).

Contact angles were determined using a Ramé-Hart contact angle goniometer (model 100-22) at room temperature. Liquid droplets were laid by a Gilmont microsyringe onto the surfaces of the thin film copolymers. Advancing and receding contact angles were measured with a tilting base. Surface energies were calculated using both the geometric mean and the Lifshitz– van der Waals–acid–base (LWAB) method. Each data point is the average of 20 measurements. Deionized water, glycerol, and diiodomethane were chosen as the testing liquids and their surface energies are given in Table 1.

X-ray photoelectron spectroscopy (XPS) characterization was done with a V. G. Scientific ESCALAB 220I-XL spectrometer with monochromated Mg K α X-ray. The XPS data were acquired ata takeoff angle of 90° unless stated otherwise.

3. Surface Energy Analysis

Two approaches are employed to calculate the surface energy of a solid material: the geometric mean method^{24,25} and the three-liquid method.^{29–31} These two methods are the most widely used for surface energy analyses even though they have received many critiques.^{26–28,32–34}

The geometric mean method estimates surface energy of a solid (γ_S) as follows:

$$\gamma_{\rm L}(1 + \cos\theta) = 2(\gamma_{\rm S}^{\rm d}\gamma_{\rm L}^{\rm d})^{1/2} + 2(\gamma_{\rm S}^{\rm p}\gamma_{\rm L}^{\rm p})^{1/2}$$
(1)

where γ_L , γ_L^d , and γ_L^p are surface energies of the test liquid and γ_S^d and γ_S^p can be calculated from measured contact angles (θ). The superscript d refers to the London dispersion forces and p refers to polar forces, including all the interactions established between the solid and liquid, such as Keesom dipole–dipole, Debye dipole–induced dipole, and hydrogen bonding, etc.

The three-liquid approach expresses the total surface energy as the sum of the Lifshitz-van der Waals (γ^{LW}) and acid-base (γ^{AB}) components:

$$\gamma = \gamma^{\rm LW} + \gamma^{\rm AB} = \gamma^{\rm LW} + 2\sqrt{\gamma^+ \gamma^-} \tag{2}$$

where γ^+ is the Lewis acid (electron acceptor) component and γ^- is the Lewis base (electron donor) component of surface energy. The LW component includes London dispersion forces, Keesom dipole–dipole, and Debye induction forces. Therefore, the total surface energy and its components, γ^{LW} , γ^+ , γ^- and



Figure 1. Monomer formulas.



Figure 2. FTIR spectra of monomers and thin film copolymers for 80/10/10 ANA/AAA/6F acid system: (a) monomers and (b) thin film copolymer after 3-h reaction at 300 °C.

 γ^{AB} , can be determined from the following equation if three testing liquids are used:

$$\gamma_{\rm L}(1+\cos\theta) = 2(\sqrt{\gamma_{\rm S}^{\rm LW}\gamma_{\rm L}^{\rm LW}} + \sqrt{\gamma_{\rm S}^{+}\gamma_{\rm L}^{-}} + \sqrt{\gamma_{\rm S}^{-}\gamma_{\rm L}^{+}}) \quad (3)$$

4. Results and Discussion

4.1. Thin Film Copolymerization with Monomer Compositions of ANA/AAA/6F Acid and ANA/HQAT/6F Acid. Two series of aromatic thermotropic LCPs were prepared: one from ANA, AAA, and 6F acid and the other from ANA, HQAT, and 6F acid. Four monomer molar compositions were chosen: 90/5/5, 80/10/10, 60/20/20, and 40/30/30. Figure 1 depicts these monomer structures.

ANA and AAA are two of the most commonly used monomers for synthesizing main-chain thermotropic LCPs. For example, two commercially available LCP products, Vectra A and B, produced by Hoechst Celanese, are made from 27/73 ANA/ABA (*p*-acetoxybenzoic acid) and 60/20/20 ANA/AAA/ TA (terephthalic acid), respectively. ANA has a side-step (crankshaft) naphthoic ring and a large L/D chain characteristic which make ANA potentially acting as a mesogenic unit. Monomers containing hydroquinone yielded the first thermotropic LCP because of its straightness and rigidity³⁵ and have been used extensively for new LCPs.^{21,22,36} In this study, AAA and HQAT also provide equal moles of acetoxy groups to react with carboxyl groups in 6F acid. Besides ester groups being formed in the resultant copolymers, AAA moiety also creates amide-bridging groups.

4.2. Characterizations of Thin Film Copolymers. Figure 2 shows typical FTIR spectra of the monomer mixtures and thin film copolymers, using 80/10/10 ANA/AAA/6F acid reaction system as an example. In Figure 2a, the band at 1679 cm⁻¹ is $\nu_{C=0}$ of the -COOH group and the band at 1761 cm⁻¹



Figure 3. TGA results of thin film copolymers (after 3-h reaction at 300 °C).



Figure 4. Surface energy comparisons between geometric mean method and LWAB methods.

TABLE 2: Contact Angles of ANA/AAA/6F Acid Thin Film Copolymers (reacted at 300 $^{\circ}$ C for 3 h)

monomer				
ratios	contact angles	water	glycerol	diiodomethane
90/5/5	advancing angle	93.3 ± 1.6	84.8 ± 2.0	44.9 ± 1.3
	receding angle	74.3 ± 2.2	56.7 ± 1.7	24.0 ± 1.2
80/10/10	advancing angle	92.5 ± 1.6	87.4 ± 2.0	50.7 ± 1.8
	receding angle	73.7 ± 1.5	59.0 ± 1.8	30.6 ± 1.8
60/20/20	advancing angle	91.9 ± 1.7	89.7 ± 2.0	50.9 ± 2.0
	receding angle	76.6 ± 2.0	70.4 ± 2.0	31.1 ± 2.3
40/30/30	advancing angle	90.9 ± 1.6	84.5 ± 1.6	53.1 ± 2.1
	receding angle	76.1 ± 1.7	61.7 ± 1.8	30.6 ± 1.7

is $\nu_{C=0}$ of the CH₃COO- group. After 3-h reaction at 300 °C, the bands at 1679 and 1761 cm⁻¹ almost completely disappear, indicating that nearly all acetoxy and carboxyl groups have been consumed and a substantial number of ester groups form at band of 1735 cm⁻¹ as shown in Figure 2b. These spectra confirm that copolymers are obtained after thin film polymerization.

TGA was used to characterize the thermostability of the thin film copolymers. Figure 3 shows TGA curves in air of ANA/ AAA/6F acid and ANA/HQAT/6F acid thin film copolymers, both with an 80/10/10 monomer mole ratio. From the curves, the 5% weight loss for the ANA/AAA/6F acid and ANA/HQAT/ 6F acid copolymers are 509 and 490 °C, respectively. These high temperatures further confirm that the thin film polymerization products are copolymers, without any oligomers remaining. Both DSC and MDSC were used to analyze the thin film copolymers. However, no obvious transition peaks were found.

The inherent viscosity of ANA/HQAT/6F acid copolymers with an 80/10/10 monomer ratio was tested in 3,5-bis(trifluoromethyl)phenol at 25 °C. The IV value is 2.5, indicating that the thin film product is indeed a copolymer. The IV value is also acceptable in terms of LCP synthesis,^{21,37} and even higher values could be obtained if increasing reaction temperature or prolonging reaction time.¹⁵

TABLE 3: Contact Angles of ANA/HQAT/6F Acid ThinFilm Copolymers (reacted at 300 °C for 3 h)

monomer				
ratios	contact angles	water	glycerol	diiodomethane
90/5/5	advancing angle	89.1 ± 1.2	78.9 ± 2.0	47.2 ± 1.7
	receding angle	72.4 ± 2.3	55.6 ± 1.9	29.3 ± 2.5
80/10/10	advancing angle	88.1 ± 1.4	84.9 ± 1.9	53.5 ± 2.1
	receding angle	76.5 ± 1.7	63.3 ± 1.7	32.3 ± 2.4
60/20/20	advancing angle	94.6 ± 2.1	89.5 ± 2.0	58.3 ± 1.8
	receding angle	79.0 ± 1.6	68.9 ± 2.3	36.7 ± 2.0
40/30/30	advancing angle	96.8 ± 1.9	88.4 ± 2.0	60.6 ± 2.3
	receding angle	82.8 ± 2.1	67.1 ± 2.3	39.0 ± 2.0

 TABLE 4: Surface Energies of ANA/AAA/6F Acid Thin

 Film Copolymers Using the Two-Liquid Geometric Mean

 Method (reacted at 300 °C for 3 h)

		γ^{d}	γ^{p}	γ
		(mJ/m^2)	(mJ/m^2)	(mJ/m^2)
90/5/5	water-diiodomethane	36.58	0.72	37.30
	glycerol-diiodomethane	35.97	0.00	35.97
	average	36.28	0.36	36.63
80/10/10	water-diiodomethane	32.60	1.31	33.90
	glycerol-diiodomethane	32.96	0.00	32.96
	average	32.78	0.65	33.43
60/20/20	water-diiodomethane	32.33	1.47	33.79
	glycerol-diiodomethane	31.81	0.00	31.81
	average	32.07	0.73	32.80
40/30/30	water-diiodomethane	30.63	1.96	32.59
	glycerol-diiodomethane	33.48	0.00	33.48
	average	32.05	0.98	33.04

Investigation based on a polarized microscope indicates that 60/20/20 and 40/30/30 ANA/AAA/6F acid and 40/30/30 ANA/ HQAT/6F acid copolymers are amorphous, while 90/5/5 and 80/10/10 ANA/AAA/6F acid and 80/10/10 and 60/20/20 ANA/ HQAT/6F acid undergo morphological evolution during reaction as follows: generation of liquid crystal phase, coalescence of liquid crystal domains, formation of schlieren texture, annihilation of disclinations, and appearance of crystalline texture. Only 90/5/5 ANA/HQAT/6F acid yields a polymer with the liquid crystalline texture. The above observation implies that -O-Ar-O- units in the HQAT moiety have greater possibility to form LC than that -O-Ar-N- units in the AAA moiety. This was coincided with He and Windle's prediction.³⁸ Comparing the rotation potential of the amide with that of the ester, they found the potential barrier between the trans and cis barriers was higher for the amide than for the ester. However, the energy difference between trans and cis conformations is more important in influencing the persistence length (or mesogenicity) and it was found larger in the ester group than in the amide group. In other words, the ester group in polyester will have a longer persistence length that is favorable to LC formation.

4.3. Contact Angles and Surface Energies of the Thin Film Copolymers. Tables 2 and 3 summarize all the advancing and receding contact angles as well as their standard deviations of the thin film copolymers for both systems as a function of monomer ratio, respectively. Since the advancing contact angle represents more precisely the equilibrium contact angle than the receding angle, only the advancing contact angle will be discussed hereafter. Table 2 indicates that at an increase in 6F

TABLE 6: Surface Energies of ANA/HQAT/6F Acid Thin Film Copolymers Using the Two-Liquid Geometric Mean Method (reacted at 300 $^{\circ}$ C for 3 h)

		$\gamma^{\mathbf{d}}$	γ^{p}	γ
		(mJ/m^2)	$(m\dot{J}/m^2)$	(mJ/m^2)
90/5/5	water-diiodomethane	33.95	1.87	35.82
	glycerol-diiodomethane	37.14	0.00	37.14
	average	35.55	0.94	36.48
80/10/10	water-diiodomethane	29.63	2.92	32.55
	glycerol-diiodomethane	33.14	0.00	33.14
	average	31.38	1.46	32.55
60/20/20	water-diiodomethane	28.06	1.51	29.57
	glycerol-diiodomethane	29.51	0.00	29.51
	average	28.78	0.76	29.54
40/30/30	water-diiodomethane	27.00	1.21	28.21
	glycerol-diiodomethane	29.16	0.00	29.16
	average	28.08	0.60	28.69

acid content from 5 to 30 mol % in the ANA/AAA/6F acid system, the advancing angle of diiodomethane increases from 45° to 53°, whereas the advancing angles of water decrease very slightly. Similar trends are found for diiodomethane in the ANA/HQAT/6F acid system as tabulated in Table 3. However, increases in the advancing angles of water and glycerol are noticed for the ANA/HQAT/6F acid copolymers. Both copolymers show nonpolar surfaces because of their large water contact angles. The increasing contact angles of both water and diiodomethane with increasing 6F acid content in the ANA/HQAT/6F acid system imply that the copolymer surfaces have been fluorinated. Similar results were reported for other copolymers by Kim¹⁰ and Chapman.⁵

Tables 4 and 5 summarize the surface energy results for the ANA/AAA/6F acid system using the two-liquid geometric mean method and three-liquid Lifshitz—van der Waals—acid—base (LWAB) method, respectively, while Tables 6 and 7 list results for the ANA/HQAT/6F acid system. Both methods yield similar values and trends on the overall surface energy.

For the ANA/AAA/6F acid system, with an increase in 6F acid content from 5 to 10% (mol), the total surface energy decreases abruptly from 37 to 34 mJ/m². Further increase in 6F acid content from 10 to 30 mol % results in little change in the surface energy, which is maintained at about 33 mJ/m². For the ANA/HQAT/6F acid system, the situation changes. Its total surface energy decreases continuously with an increase in the content of 6F acid monomer. Figure 3 compares the surface energies calculated from both the two-liquid geometric mean method and the three-liquid LWAB method for both ANA/AAA/6F acid and ANA/HQAT/6F acid systems. The agreement of surface energy calculated from these two methods is excellent with about 1% difference.

Negative square root values of the Lewis acid components (γ^+) of surface energies are found in this study. According to Good and van Oss,³¹ these negative values could be assumed to be zero when they are small, which leads to a vanishing value of the donor-acceptor component. As a result, the acid-base interactions, γ^{AB} , for these two polymer systems are trivial and the total surface energies are mainly contributed from γ^{LW} . Because of containing a large amount of aromatic rings and >C=O groups in polymeric chains, both ANA/AAA/6F acid

TABLE 5: Surface Energies of ANA/AAA/6F Acid Thin Film Copolymers Using the Three-Liquid LWAB Method (reacted at 300 °C for 3 h)

		$\gamma^+ (mJ/m^2)$	γ^{-} (mJ/m ²)	$\gamma^{AB} (mJ/m^2)$	$\gamma^{LW} (mJ/m^2)$	γ (mJ/m ²)
90/5/5	water-glycerol-diiodomethane	0.00	2.80	0.00	37.09	37.09
80/10/10	water-glycerol-diiodomethane	0.00	4.58	0.00	33.90	33.90
60/20/20	water-glycerol-diiodomethane	0.00	6.12	0.00	33.79	33.79
40/30/30	water-glycerol-diiodomethane	0.00	4.59	0.00	32.56	32.56

TABLE 7: Surface Energies of ANA/HQAT/6F Acid Thin Film Copolymers Using the Three-Liquid LWAB Method (reacted at 300 °C for 3 h)

		γ^+ (mJ/m ²)	γ^{-} (mJ/m ²)	γ^{AB} (mJ/m ²)	γ^{LW} (mJ/m ²)	γ (mJ/m ²)
90/5/5	water-glycerol-diiodomethane	0.00	3.39	0.00	35.82	35.82
80/10/10	water-glycerol-diiodomethane	0.00	7.09	0.00	32.29	32.29
60/20/20	water-glycerol-diiodomethane	0.00	4.29	0.00	29.56	29.56
40/30/30	water-glycerol-diiodomethane	0.00	2.62	0.00	28.21	28.21

 TABLE 8: XPS Atomic Concentration of the Thin Film

 Copolymers

monomer	exper	imental	XPS (A	AT%)	theoretical values			es
ratios	С	0	Ν	F	С	0	Ν	F
	ANA/AAA/6F Acid							
90/5/5	79.00	14.06	0.57	6.37	82.77	14.61	0.37	2.25
80/10/10	72.28	13.90	2.00	11.84	81.02	13.87	0.73	4.38
60/20/20	73.45	10.88	1.78	13.89	77.78	12.50	1.39	8.33
40/30/30	73.41	10.86	1.72	14.01	74.83	11.26	1.99	11.92
		A	NA/HQ	QAT/6F	Acid			
90/5/5	80.95	14.06	/	4.98	82.77	14.98	/	2.25
80/10/10	78.90	14.33	/	6.77	81.02	14.60	/	4.38
60/20/20	78.78	11.84	/	9.38	77.78	13.89	/	8.33
40/30/30	75.70	12.41	/	11.89	74.83	13.25	/	11.92

and ANA/HQAT/6F acid copolymers show the Lewis base (electron donor) character.

4.4. XPS Study of the Thin Film Copolymers. To confirm our hypothesis that the variation of surface energy with 6F acid content is due to preferential enrichment of bulky $-C(CF_3)_2$ at the air-polymer interface because of chain conformation and packaging, XPS at a takeoff angle of 90° was employed to study the interface chemistry. For the ANA/AAA/6F acid system, Table 8 shows that experimental atomic concentrations of F element at interface far exceed the corresponding to theoretic (bulk) values. The F content at the interface increases rapidly from 6.37 to 11.84% when the 6F acid concentration increases from 5 to 10 mol %. Interestingly, the C% and O% at the interface decrease with increasing 6F acid in this composition range, suggesting preferential surface segregation or enrichment of fluorocarbons against C and O at the interface. With further increase in 6F acid in the copolymers, the experimental F value varies, in a much slower pace, from 11.8 to 14.0%, while there are little changes in C% and O% content at the surface.

For the ANA/HQAT/6F acid system, the atomic concentration of F element at the surface increases almost linearly with an increase in the 6F acid monomer ratio. These XPS results agree well with their surface energy values, which decreased consistently with an increase in fluorine content. A smaller takeoff angle (30°) was also utilized to re-confirm the surface chemistry profiles on an 80/10/10 ANA/HQAT/6F acid thin film copolymer. It is well-accepted that the takeoff angle corresponds to the depth of the polymer surface at the air-polymer interface: ^{10,39} the smaller the takeoff angle, the nearer to the surface. The experimental atomic concentrations of F element taken at 30° and 90° are 9.71 and 6.77%, respectively. These results clearly verify that the nearer to the surface, the more fluorine exists, indicating the pendant CF3 segments originating from 6F acid is preferentially enriched to the outermost layer at the airpolymer interface against other elements. In other words, the presence of the bulky $-C(CF_3)_2$ groups in the bis(benzoic acid) moiety hinders intrasegmental mobility and thus stiffens the backbone chains. The bulky $-C(CF_3)_2$ – groups also inhibit intersegmental chain packing, thus leading themselves to preferentially enrich at the air-polymer interface in order to reduce the overall Gibbs free energy.

The different relationships between surface energy and 6F acid content for ANA/AAA/6F acid and ANA/HQAT/6F acid

systems, as shown in Tables 4 and 5, may be explainable with the aid of XPS data. The difference may mainly arise from two factors: different chain rigidities between AAA and HQAT moieties and hydrogen bonding induced by the amide group because of the AAA moiety. Since the rigidity of -O-Ar-N- units in AAA is lower than that of -O-Ar-O- units in HQAT, the pendant CF₃ segments in the former system has a greater possibility to be able to preferential reside at the airpolymer interface than the latter system. Therefore, the atomic concentrations of F element measured by XPS are greater in the ANA/AAA/6F acid system than that in the ANA/HQAT/ 6F acid system, as shown in Table 8. It is very interesting to point out that the atomic concentrations of F element in ANA/ HQAT/6F acid copolymers are close to their bulk values, especially for 60/20/20 and 40/30/30 monomer ratios, implying the embedding of $-C(CF_3)_2$ groups in the bulk possibly caused by the high rigidity of -O-Ar-O- units in HQAT.

Even though the ANA/AAA/6F acid copolymer has greater fluorine enrichment at the air-polymer interface than the ANA/ HQAT/6F acid copolymer, they follow different patterns with an increase in the 6F acid content. The surface energy of the former drops significantly when the 6F acid content increases from 5 to 10% (mol), but it then becomes invariant with further increasing in 6F acid content, whereas the latter system decreases continuously. This is may be due to the fact that the amide groups in the ANA/AAA/6F acid copolymer play an important role on surface energy because amide induces strong intermolecular hydrogen bonding. Evidence of strong hydrogen bonding can be observed from the water contact angles, shown in Table 3. Even with the interference of nonpolar perfluorocarbon moiety, the water contact angle still shows a clear decreasing trend with an increase in the amide content, which is consistent with the 6F acid content. In contrast, the ANA/ HQAT/6F acid system does not have hydrogen bonding and its water contact angle tends to increase with increasing the 6F acid content.

5. Conclusions

Thin film polymerization technique was utilized to synthesize two series of liquid crystalline/crystalline copolymers with - $C(CF_3)_2$ – in the main chain. Surface energies were found in the range of 28-36 mJ/m² depending on the monomer concentrations and reaction systems. For the ANA/AAA/6F acid system, an increase in 6F acid content from 5 to 10% (mol), the surface energy decreased. But a further increase in 6F acid content resulted in little change in the surface energy and it was maintained at about 33 mJ/m². For the ANA/HQAT/6F acid system, the surface energy decreased continuously with an increase in the content of 6F acid. XPS data were in agreement with the surface energy behavior of the two series of copolymers. The difference between the ANA/AAA/6F acid and ANA/ HQAT/6F acid systems can be explained through higher chain rigidity and the existence of hydrogen bonding in the former system.

Acknowledgment. The authors express their gratitude to the Institute of Materials Research and Engineering (IMRE), Singapore, for financial support and the National University of Singapore (NUS) with Research Fund No. R-279-000-048-112. Special thanks go to Ms. S. X. Cheng and Dr. C. B. He for useful discussion and Dr. S. Mullick for the provision of monomers. Thanks are also due to Mr. J. W. Chai and Dr. K. P. Pramoda at IMRE for XPS and MDSC experiments, respectively.

References and Notes

(1) Carlson, D. P.; Schmiegel, W. Ullmann's Encyclopedia of Industrial Chemistry; VCH Verlagsgesellschaft: Weinheim, 1988; p 393.

- (2) Feiring, A. E. Pure Appl. Chem. 1994, A31, 1657.
- (3) Pittman, A. G. In *Fluoropolymers*; Wall, L A., Ed.; Wiley-Interscience: New York; 1972; Chapter 1.
- (4) Van der Grinten, M. G. D.; Clough, A. S.; Shearmur, T. E.; Bongiovanni, R.; Priola, A. J. Colloid Interface Sci. **1996**, 182, 511.
- (5) Chapman, T. M.; Benrashid, R.; Marra, K. G.; Keener, J. P. Macromolecules 1995, 28, 331.
- (6) Chapman, T. M.; Marra, K. G. *Macromolecules* 1995, 28, 2081.
 (7) Marra, K. G.; Chapman, T. M.; Orban, J. M. *Macromolecules* 1996, 29, 7553.
- (8) Zhang, H.; Marra, K. G.; Ho, T.; Chapman, T. M.; Gardella Jr., J.
 A. *Macromolecules* 1996, 29, 1660.
- (9) Kim, D.; Lee, S.; Doh, K.; Nam, Y. J. Appl. Polym. Sci. **1999**, 74, 1917
- (10) Kim, D.; Lee, S.; Doh, K.; Nam, Y. J. Appl. Polym. Sci. 1999, 74, 2029.
- (11) Hwang, S. S.; Ober, C. K.; Perutz, S.; Iyengar, D. R.; Schneggenburger, L. A.; Kramer, E. J. *Polymer* **1995**, *36*, 1321.
- (12) Iyengar, D. R.; Perutz, S.; Dai, C.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1996**, *29*, 1229.
- (13) Wang, J.; Mao, G.; Ober, C. K.; Kramer, E. J. Macromolecules 1997, 30, 1906.
- (14) Cheng, S. X.; Chung, T. S.; Mullick, S. J. Polym. Sci.: Part B: Polym. Phys. 1999, 37, 3084.
- (15) Rybnikar, F.; Yuan, B. L.; Geil, P. H. Polymer 1994, 35, 1863.

- (16) Chung, T. S.; S. X. Chung. J. Polymer Sci., Chem. 2000, 38, 1257.
- (17) Chung, T. S.; Ma, K. X. J. Phys. Chem. B 1999, 103, 108.
- (18) Collyer, A. A. Liquid Crystalline Polymers: From Structures to Applications; Elsevier Science: London, 1992.
- (19) Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University Press: Cambridge, England, 1999.
- (20) Shiaev, V. P.; Lam, L. Liquid Crystalline and Mesomorphic Polymers; Springer-Verlag: New York, 1994.
- (21) Chung, T. S.; Calundann, G. W.; East, A. J. Encyclopedia Eng. Mater. 1989, 2, 625.
- (22) Chung, T. S. Polym. Eng. Sci. 1986, 26, 901.
- (23) Ueda, M.; Noguchi, Y.; Sugiyama, J.; Yonetake, K.; Masuko, T. *Macromolecules* **1992**, *25*, 7086.
- (24) Owens, D. K.; Wendt, R. C. J. Appl. Polym. Sci. 1969, 13, 1741.
 (25) Kaelble, D. H. J. Adhesion 1970, 2, 50.
- (26) Della Volpe, C.; Siboni, S. J. Adhesion Sci. Technol. 2000, 14, 235.
- (27) Garbassi, F.; Morra, M.; Occhiello, E. Polymer Surfaces: From
- Physics to Technology; John Wiley & Sons: New York, 1998.
 - (28) Fowkes, F. M. J. Adhesion Sci. Technol. 1987, 1, 7.
- (29) Van Oss, C. J.; Ju, L.; Chaudhury, M. K.; Good, R. J. J. Colloid Interface Sci. 1989, 128, 313.
- (30) Good, R. J.; van Oss, C. J. Modern Approaches to Wettability; Plenum: New York, 1991.
- (31) Good, R. J. In *Contact Angle, Wettability, and Adhesion*; VSP: Utrecht, The Netherlands, 1993.
 - (32) Mora, M. J. Colloid Interface Sci. 1996, 182, 312.
- (33) Greiveldinger, M.; Shanahan, M. E. R. J. Colloid Interface Sci. 1999, 215, 170.
- (34) Bouali, B.; Ganachaud, F.; Chapel, J. P.; Pichot, C.; Lanteri, P. J. Colloid Interface Sci. 1998, 208, 81.
- (35) Cottis, S. G.; Economy, J.; Nowak, B. E. U.S. Patent 3,637,595, 1972 (issued to Carborundum).
- (36) Makhija S.; Jaffe, M. J. Appl. Polym. Sci. 1994, 53, 609
- (37) Jaffe, M.; Chen, P.; Choe, E. W.; Chung, T. S.; Makhija, S. High Perform. Polym. Blends, High Perform. Polym. 1994, 117, 297.
- (38) He, C.; Windle, A. H. *Macromol. Theory Simul.* **1995**, *4*, 289.
 (39) Kassis, C. M.; Steehler, J. K.; Betts, D. E.; Guan, Z.; Romack, T.
- J.; DeSimone, J. M.; Linton, R. W. Macromolecules 1996, 29, 3247.