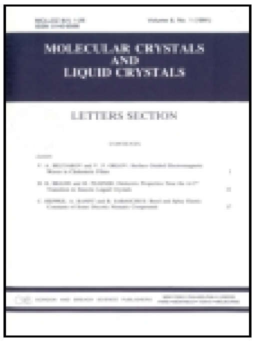

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Liquid Crystal Alignment Behaviors on Comb-Like Fluorinated Polystyrene Films

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ABSTRACT

We synthesized a series of fluorinated polystyrene (PCMSF#, # = 50, 80, and 100), where # is the molar content of 1H,1H,2H,2H-perfluorodecanethiolate moiety, using polymer analogous reactions to investigate their liquid crystal (LC) alignment properties. In general, the LC cell fabricated using the polymer film having a higher molar content of fluorinated side group showed vertical LC alignment behavior with a pretilt angle of about 90°. The vertical alignment behavior was well correlated with the surface energy value and fluorine atomic percent of these polymer films. For example, vertical alignment was observed when the surface energy values of the polymer were smaller than about 8.77 mJ/m^2 generated by the nonpolar and long fluorocarbon groups. Good electro-optical characteristics, such as voltage holding ratio (VHR) and residual DC voltage (R-DC), and aligning stabilities at 250°C were observed for the LC cells fabricated using PCMSF100 as a LC alignment layer.

KEYWORDS
Alignment; fluorine; liquid crystal; polystyrene; vertical

1. Introduction

The mechanical rubbing of polymeric surfaces is the most widely used technique to make the uniform alignment of the liquid crystal (LC) molecules in the manufacture of liquid crystal display (LCD) [1–6]. Polyimide derivatives are most commonly employed as LC alignment layers through this rubbing process, because they provide very stable LC alignment [7–16]. Polyimide derivatives having long alkyl or alkyloxy groups, such as semi-flexible copolyimides containing *n*-octadecyl side groups and polyimides with (*n*-decyloxy)biphenyloxy side groups, show vertical LC alignment behaviors [17–20]. Polystyrene (PS) derivatives having long alkyl chains can also produce vertical LC alignment layers. For example, LC cells fabricated using a nematic LC and rubbed polymer films of *n*-alkylsulfonylmethyl- and *n*-alkylthiomethyl-substituted PSs having more than 8 carbons (number of alkylcarbon > 8) show vertical LC alignment behaviors [21]. The LC cells made from the 4-alkylphenoxymethyl-substituted PSs showed vertical LC alignment behaviors even at a very high rubbing density of 250, regardless of the length of the alkyl side groups [22].

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Comb-like fluorinated polymers have been widely used in a variety of coatings, electronics, and bio-medical applications due to their excellent properties, such as low surface energy, good chemical and thermal stability, and biocompatibility [23–25]. The molecular structure of comb-like fluorinated polymer has an influence on the surface properties, such as the wetting behavior and stability [26–30]. For example, the closely packed structure of trifluoromethyl end groups in the fluorinated side chains of comb-like polymers can give lower surface energy value. In addition, the packing density of fluorinated side chains can be affected by the backbone and side chain structure of the comb-like fluorinated polymers. When the backbone structures of comb-like fluorinated polymers are identical, polymers with longer fluorinated side chains can have lower surface energy value due to their ordered side chain structures [31]. For example, poly(fluoroalkyl acrylate)s with short fluorinated side chains (number of fluorocarbon < 6) exhibits a poorly ordered state, whereas those with long side chains (number of fluorocarbon > 7) have hexagonally ordered fluorinated side chains with low surface energy.

In this study, comb-like fluorinated polystyrenes (PCMSF#) having 8 number of fluorocarbon and trifluoromethyl end groups were synthesized to increase the pretilt angle of the LCs and to study the effect of the molar contents of the side groups on the LC alignment behavior. The optical and electrical properties of the LC cells fabricated using the unrubbed or rubbed polymer films are also included.

2. Experimental part

2.1. Materials

4-Chloromethylstyrene and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol were purchased from Aldrich Chemical Co. and a nematic LC, 5CB ($n_e = 1.7360$, $n_o = 1.5442$, and $\Delta\varepsilon = 14.5$, where n_e, n_o, and $\Delta\varepsilon$ represent extraordinary refractive indexes, ordinary refractive indexes, and dielectric anisotropy, respectively), were purchased from Merck Co. *N,N′*-Dimethylacetamide (DMAc) and ethanol were dried over molecular sieves (4 Å). Tetrahydrofuran (THF) was dried by refluxing with benzophenone and sodium followed by distillation. 4-Chloromethylstyrene was purified by column chromatography on silica gel using hexane as an eluent to remove any impurities and inhibitors (*tert*-butylcatechol and nitroparaffin). Poly(4-chloromethylstyrene) (PCMS of $M_n = 21\,000$ and $M_w/M_n = 1.94$) was synthesized through conventional free radical polymerization of the 4-chloromethylstyrene using 2,2′-azoisobutyronitrile (AIBN) under a nitrogen atmosphere. AIBN (Junsei Chemical Co., Ltd.) was used as an initiator. The AIBN was purified from crystallization using methanol. The sodium *n*-fluoroalkanethiolates were prepared. All other reagents and solvents were used as received.

2.2. Preparation of poly[p-[[(perfluorooctylethylene)thio]methyl]styrene]

The following procedure was used to synthesize all of the 1*H*,1*H*,2*H*,2*H*-perfluorodecanethioethermethyl-substituted polystyrenes, PCMSF#, where # represent the molar content (%) of perfluorodecane thiolate moiety in the side group. The synthesis of the 1*H*,1*H*,2*H*,2*H*-perfluorodecanethioethermethyl-substituted polystyrene (PCMSF100) is given as an example. PCMS (1.0 g, 6.58 mmol) was dissolved in *N,N′*-dimethylacetamide (DMAc, 20 mL) and sodium 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiolate (3.304 g, 6.58 mmol,

Table 1. Reaction conditions and results for the synthesis of the PCMS and PCMSF#.

Polymer designation	Sodium perflurodecane thiolate (mol%)	Degree of substitution (%)	M_n[a]	M_w/M_n[a]
PCMS	–	–	21000	1.94
PCMSF50	50	50	30800	1.62
PCMSF80	80	80	33500	1.63
PCMSF100	100	100	36600	1.59

[a] Obtained from GPC using THF as solvent with respect to monodisperse polystyrene as standard.

100 mol% compared with PCMS) was added. The mixture solution in DMAc was magnetically stirred at 40°C for 30 min under a nitrogen atmosphere. The reaction conditions are listed in Table 1. The solution mixture was cooled to room temperature and then poured into methanol to obtain a white precipitate. The precipitate was further purified by several reprecipitations from DMAc solution into methanol and then washed with hot methanol to remove the sodium methoxide and remaining salts. The PCMSF100 was obtained in yields above 80% after drying overnight in a vacuum. The degree of substitution of the chloromethyl to the 1*H*,1*H*,2*H*,2*H*-perfluorodecanethioethermethyl group was calculated by comparing the singlet at 1.0–2.0 ppm (3H) with the backbone peak at 3.5–3.9 ppm (2H) which includes the contribution of residual poly(chloromethylstyrene) and was found to be almost 100% within experimental error.

PCMSF100 ^{1}H NMR ($CDCl_3$): $\delta = 1.38$ (2H), 1.71 (1H), 2.34 (2H), 2.60 (2H), 3.65 (2H), 6.45 (2H), 6.97 (2H).

The copolymers of PCMSF100, designated as PCMSF#, where # is the degree (%) of substitution of the chloromethyl to the 1*H*,1*H*,2*H*,2*H*-perfluorodecanethioethermethyl group, were prepared from the same procedure, which was used for PCMSF100, except that 100 mole% of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol was used. The amounts of sodium perfluorodecanethiolate used for the preparation of PCMSF50, and PCMSF80 are listed in Table 1.

2.3. *Film preparation and LC alignment process*

Solutions of PCMSF# in 1:1 chloroform and 1,1,2-trichlorotrifluoroethane (2 wt%) were prepared, respectively. These solutions were filtered using a PTFE membrane with a pore size of 0.45 μm. Thin films of the polymers were prepared by spin-coating (2000 rpm, 30 sec) onto ITO coated glass substrates, followed by the drying at 80°C for 10 min. The film thicknesses on glass substrates were measured using a variable-angle multi wavelength ellipsometer (L2W15S830, Stokes Waferskan Ellipsometer) and were found to be about 500 nm within an experimental error of ± 10%. The polymer films were rubbed using a rubbing machine (RMS-50-M, Nam Il Optical Components Corp.) wrapped by velvet cloth; number of rubbing and rubbing depth were 1 and 0.5 mm, respectively.

2.4. *LC cell assembly*

Antiparallel LC cells were fabricated using the unrubbed or rubbed polymer film onto ITO coated glass slides. The antiparallel LC cells were constructed by assembling the films together antiparallel with respect to the rubbing direction using spacers with thicknesses of 6.5 μm and 50 μm. The cells were filled with nematic LC, 5CB. The manufactured LC cells were sealed with epoxy glue.

2.5. Instrumentation

The ^{1}H NMR measurements were carried out on a Bruker AVANCE spectrometer at 300 MHz. The gel permeation chromatography (GPC) was used to measure the number average molecular weight (M_n) and polydispersity index (M_w/M_n) of the synthesized polymer with respect to PS standards using tetrahydrofuran (THF) as the eluent and an UV detector. The optical transmittance of the polymer films onto ITO coated glass substrates was obtained using UV-Vis spectroscopy (Perkin Elmer Lamda 20 spectrometer). The electron spectroscopy for chemical analysis (ESCA) experiment was performed in an UHV multipurpose surface analysis system (Thermo Scientific, SIGMA PROBE, UK) operating at base pressures $< 10^{-10}$ mbar. The photoelectron spectra were excited by an Al K_α (1486.6 eV) anode operating at constant power of 100 W (15 kV and 10 mA). During the spectra acquisition, the constant analyzer energy (CAE) mode was employed at a pass energy of 40 eV and a step of 0.1 eV at a take-off angle of 90°. The binding energy (BE) scale was calibrated from the hydrocarbon contamination using the C_{1s} peak at 285.0 eV. Core peaks were analyzed using a linear-type background, and peak positions and areas were obtained using fitting program (Thermo Scientific, Avantage Data System) by a least-square fitting of model curves (70% Gaussian, 30% Lorentzian) to the experimental data. The contact angles of distilled water and methylene iodide on the polymer films were determined with a Kruss DSA10 contact angle analyzer equipped with drop shape analysis software. The surface energy value was calculated using the Owens-Wendt's equation as

$$\gamma_{sl} = \gamma_s + \gamma_l - 2({\gamma_s}^d{\gamma_l}^d)^{1/2} - 2({\gamma_s}^p{\gamma_l}^p)^{1/2}$$

where γ_l is the surface energy of the liquid, γ_{sl} is the interfacial energy of the solid/liquid interface, γ_s is the surface energy of the solid, γ_l^d and γ_l^p are known for the test liquids, γ_s^d and γ_s^p can be calculated from the measured static contact angles [32]. The LC alignment direction of the antiparallel LC cells was investigated by measuring the angular dependence of the absorbance of a dichroic dye (disperse blue 1) dissolved in 5CB at a concentration of 1 wt% on the rotation angle of the samples using optical apparatus equipped with a He-Ne laser, a polarizer, and a photodiode detector [6]. The pretilt angle of the antiparallel LC cells was measured by the crystal rotation method [33]. The cell gap was measured before filling the LCs using a spectrophotometer (Ocean Optics Inc., S2000). The polarized optical microscopy (POM) images of the LC cell were taken using an optical microscopy (Nikon, ECLIPSE E600 POL) equipped with a polarizer and digital camera (Nikon, COOLPIX995). The voltage holding ratio (VHR) was measured using a VHR measurement system (autronic-MELCHERS, VHRM 105). The pulse width, frame frequency, and data voltages were 64 μs, 60 Hz, and 1.0 V, respectively. The measurement temperatures were 25 and 60°C. The residual DC voltage (R-DC) value was evaluated using a capacitance-voltage (C-V) hysteresis method, defined as the depletion width difference between reverse and forward direction scans, which is used by Nissan Chemical Industries, Ltd. The capacitance was recorded by sweeping DC voltage in a range of −10V and 10V at 1 kHz using C-V method. The measurement temperatures were 25°C.

3. Results and discussion

Figure 1 shows the synthetic routes to the 1*H*,1*H*,2*H*,2*H*-perfluorodecanethioethermethyl-substituted polystyrenes (PCMSF100) and copolymers (PCMSF50 and PCMSF80, where # is the molar content (%) of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethioethermethyl side groups).

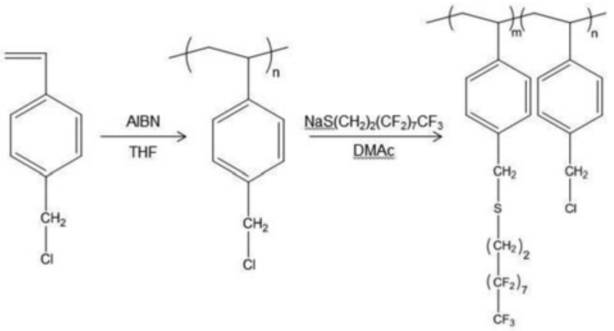

Figure 1. Synthetic route of fluorinated polystyrene films (PCMSF#), where # indicate the mole percent of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiolate containing monomeric units in the polymer.

The copolymers with different degrees (%) of substitution were obtained by varying the amounts of sodium perfluorodecane thiolate in the reaction. Almost 100% conversions from chloromethyl to 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiolate were obtained, when 100 mol% of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol was used at 40°C for 30 min. The average molecular weights (M_n) of these polymer series synthesized from the PCMS ($M_n = 21\ 000$) were always larger than 30,000 indicating that polymer modification from PCMS to the polymers in this paper gave rise to increase of average molecular weights of polymers, as expected (Table 1). Quantitative analysis of transparency of PCMSF# films was evaluated using UV-Vis spectra to investigate the possibility for the surface coating applications. The transmittance value of the coated PCMSF# film onto glass substrate is in range of 88–89% at 550 nm, which is similar with that of bare glass substrate. Conclusively, the optical transparency of the PCMSF# film in the visible light region is good enough to be used as optical materials for display devices.

At first the LC alignment behaviors of the LC cells fabricated with the unrubbed PCMSF# films were investigated (Fig. 2). Random planar LC alignment was observed for the LC cells fabricated using the unrubbed PCMS film. When the molar content of the perfluorodecane thioethermethyl containing monomeric unit in the PCMSF# was less than 80%, the LC cells fabricated with the unrubbed PCMSF# film showed poor LC alignment in the conoscopic images. On the other hand, the polarized optical microscopy (POM) images and polar diagrams of the absorbance of a dichroic dye (disperse blue 1) in the antiparallel LC cells fabricated using 5CB and the unrubbed polymer films of the PCMSF100, which show vertical LC alignment, were observed, respectively. All of the PCMSF100 films were able to produce stable vertical LC alignment layers and the vertical LC alignment was maintained for at least more than several months since we first made the LC cells from these polymers. Therefore, as the molar content of the perfluorodecane thioethermethyl side groups increases, the vertical LC aligning ability of the LC cell increases.

The pretilt angles of the antiparallel LC cells fabricated with the PCMSF100 films using 5CB were measured to study the effect of the number of rubbing on the LC alignment direction (Fig. 3). The pretilt angle on the unrubbed PCMSF100 film was about 90°. The pretilt angles of the LC cells fabricated with the rubbed PCMSF100 films were found to decrease as the number of rubbing is increased from 0 to 5, as expected. For example, the pretilt angles of PCMSF100 decrease from 90° to 89°, respectively. Therefore, the LC cells fabricated from the 1*H*,1*H*,2*H*,2*H*-perfluorodecanethioethermethyl-substituted PSs maintain their high pretilt angles even at a very high number of rubbing.

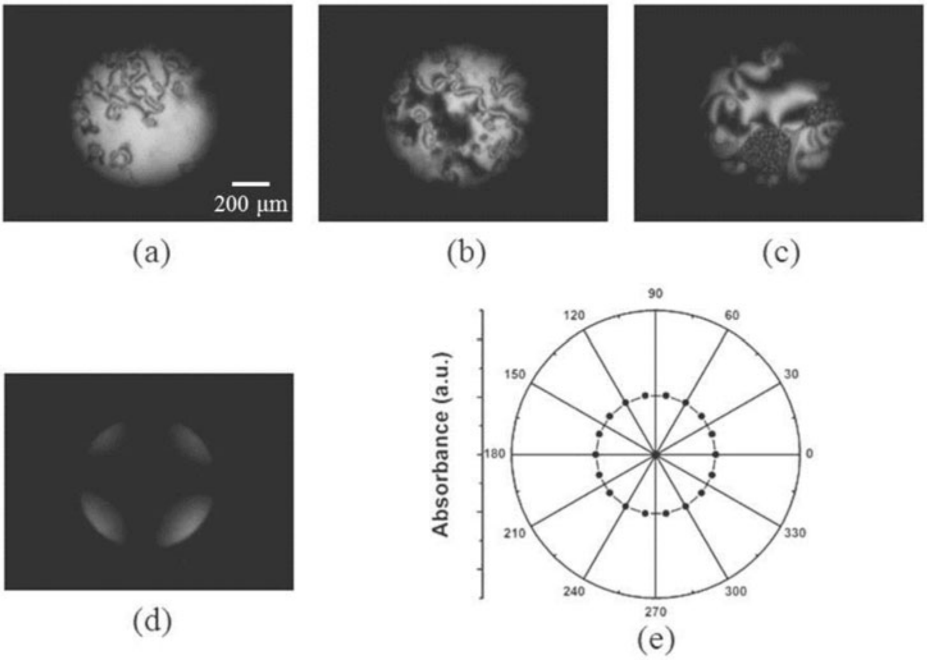

Figure 2. POM images of the antiparallel LC cell made from (a) PCMS, (b) PCMSF50, (c) PCMSF80, and (d) PCMSF100 films, and (e) polar diagrams of the absorbance of a dichroic dye (disperse blue 1) in antiparallel LC cells made from PCMSF100 films using 5CB as a function of rotation angle of samples.

Based on the results obtained for the LC alignment behavior and the pretilt angle, we found a general trend that the polymers having higher molar contents of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethioethermethyl side groups have a preference for vertical LC alignment. It would be expected for such polymers to have a lower surface energy (or lower surface polarity) [34]. Figure 4 and Table 2 shows the surface energy values of the polymer films obtained based on the static contact angles of water and methylene iodide. The total surface energy

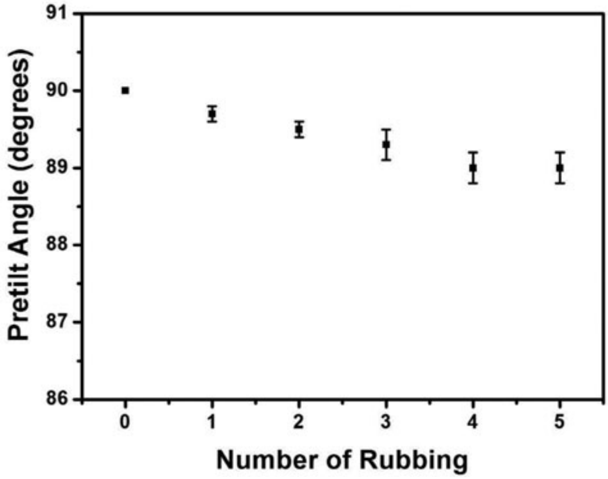

Figure 3. Pretilt angles of the antiparallel LC cells fabricated with rubbed PCMSF100 films as a function of number of rubbing.

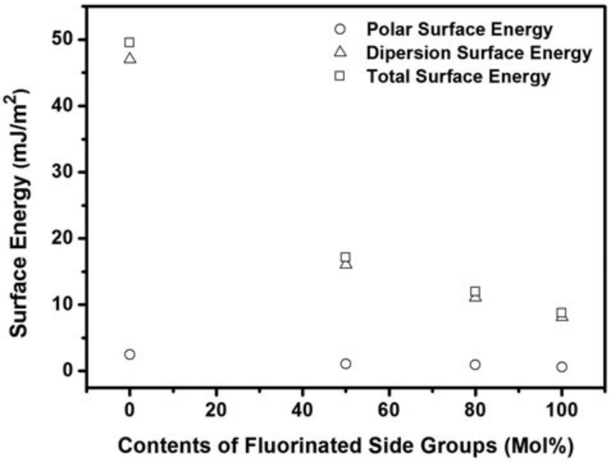

Figure 4. Surface energy values of PCMSF# films according to the molar content of the 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiolate moiety in the side groups.

was calculated using the Owens-Wendt's equation and this value is a summation of the polar and dispersion contributions. The total surface energy values of PCMSF50, PCMSF80, and PCMSF100 were found to be very low, viz. 17.14, 12.00, and 8.77 mJ/m^2, respectively. Polyimides with fluorinated side groups have been widely used to obtain LCs aligned vertically to the alignment layer surface, because their fluorinated side groups can produce low surface energy layers due to their ordered side chain structures [31]. For the same reason, the LC cells fabricated from PCMSF100 having a lower total surface energy show very stable vertical LC alignment with a pretilt angle of about 90°. We also found that there are critical surface energy values of the polymers to give vertical LC alignment behavior. The vertical LC alignment was observed from the PCMSF100 films. The total surface energy values of this polymers is 8.77 mJ/m^2, whereas the other polymer having total surface energy values larger than about 12.00 mJ/m^2 such as PCMS (49.51 mJ/m^2) and PCMSF50 (17.14 mJ/m^2) and PCMSF80 (12.00 mJ/m^2) did not show vertical alignment behavior.

We performed ESCA studies of the PCMSF# films in order to measure the chemical composition of the polymer surfaces. Figure 5 shows the ESCA spectra of F recorded at 90° take-off angle. ESCA spectra were fitted to Gaussian-Lorentzian sum functions and the full width at half maximum (FWHM) was kept below at about 1.6 keV. Distinct one signal was observed in the F_{1s} ESCA spectra and was assigned to the component C-F at 687 eV. Since 1*H*,1*H*,2*H*,2*H*-perfluorodecanethioethermethyl unit 17 fluorine atoms, the increase of the perfluorodecanethiomethyl content in the polymer increases the intensity of *C–F* peak as shown in Figure 5(a).

Table 2. Surface energy values and LC alignment properties of the polymers.

	Contact angle (o)[a]		Surface energy (mJ/m^2)[b]			
Polymer designation	Water	Methylene iodide	Polar	Dispersion	Total	Vertical LC aligning ability[c]
PCMS	82	14	2.48	47.03	49.51	X
PCMSF50	108	81	1.09	16.04	17.14	X
PCMSF80	114	92	0.93	11.08	12.00	X
PCMSF100	120	100	0.61	8.16	8.77	O

[a] Measured from static contact angles.
[b] Calculated from Owens-Wendt's equation.
[c] Circle (O) and cross (X) indicate unrubbed polymer film have vertical and random planar LC aligning ability, respectively.

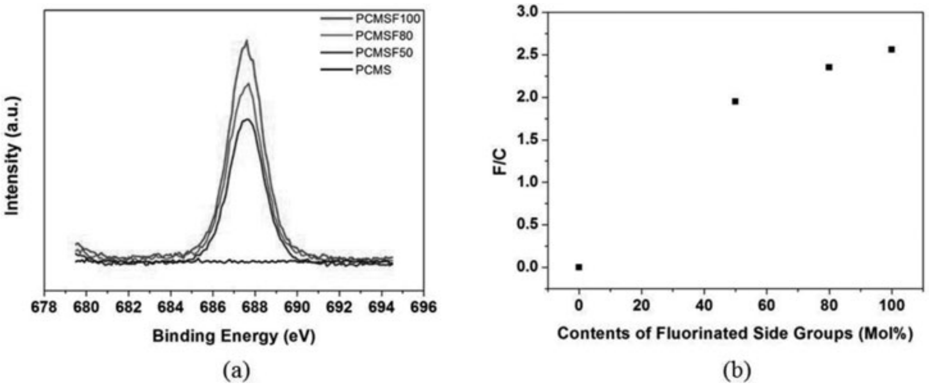

Figure 5. ESCA spectra of (a) F recorded at 90° take-off angle and (b) atomic ratio (F/C) of PCMSF# films according to the molar content of the 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiolate moiety in the side groups.

Since PCMS does not contain any fluorine atom, F peak should not be observed form the ESCA spectrum of PCMS. It was also noted that the experimental fluorine atomic percent values are always larger than the theoretical values. Possibly more hydrophobic perfluorine units in the polymers are preferentially located on the surface during the film coating process. Similarly, others also reported the larger content of fluorine groups on the polymer surface from ESCA studies [35].

The thermal stability of the LC cell made from the PCMSF100 film was estimated from the POM image after heating for 1 h at 100, 200, and 250°C, respectively. As shown in Figure 6, the distinguishable difference of pretilt angle on PCMSF100 film having vertical LC aligning ability cannot be observed through Maltese cross pattern in conoscopic POM images, indicating that the vertical LC aligning ability of the PCMSF100 LC cell was found to be maintained even at the high temperature. The total surface energy values of the PCMSF100 films obtained based on the static contact angles of water and methylene iodide were also measured after heating. When the temperature increased to 250°C, total surface energy value, one of the film properties, of the PCMSF100 film was maintained in the range of about 8–9 mJ/m^2. The electro-optical (E-O) performance of the LC cell fabricated with the PCMSF100 film was measured for the possible practical LC display application. The LC cell exhibited a voltage holding ratio (VHR) of above 99% at 25°C and this value was maintained at 60°C. It is sufficiently high for practical applications as the LC alignment layer in TFT addressed LCD [1]. The residual DC voltage (R-DC) of the LC cell measured using the capacitance–voltage (C–V) hysteresis method was found to be very low, about 10 mV, which is even smaller than that of commercial polyimides [1]. The excellent thermal stability, VHR, and R-DC of the LC cell made from PCMSF100 film was ascribed to the intrinsic property of the fluorinated polymers such as good thermal stability and low dielectric constant [24, 36].

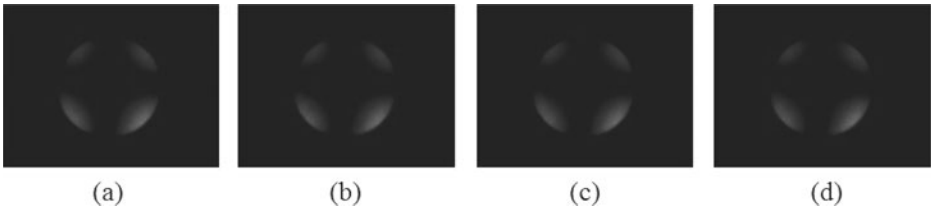
(a) (b) (c) (d)

Figure 6. POM images of the LC cells made from rubbed PCMSF100 films with annealed for 1 h at (a) room temperature, (b) 100°C, (c) 200°C, and (d) 250°C.

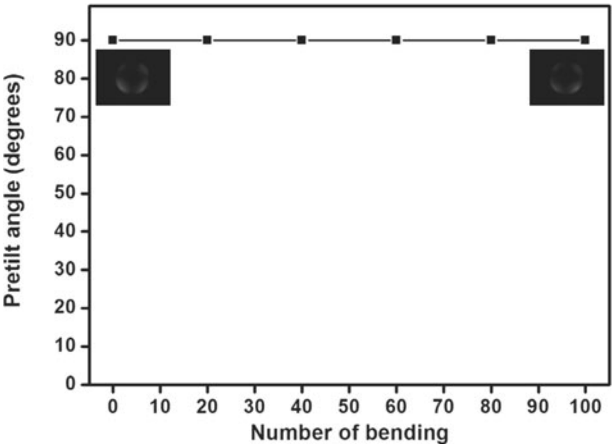

Figure 7. Pretilt angles of the LC cell made from PCMSF100 film on PET substrate as a function of number of bending.

Recently, considerable effort has been made to develop plastic substrates for flexible LC displays [37]. All of the LC cells made from the unrubbed PCMSF# films on polyethylene terephthalate (PET) substrates exhibit similar LC alignment behavior compared with the LC cells made from same polymer films on ITO substrates as previously shown in Figure 2. We found that the LC cells fabricated using the unrubbed PCMSF100 film on plastic *PET* substrates show vertical LC alignment behavior. Furthermore, this LC cell showed very nice vertical LC aligning ability with a high pretilt angle of about 90° which was maintained after bending it 100 times (Fig. 7). Therefore, PCMSF100 can be considered as candidate LC alignment layers for flexible LC displays, such as in vertical alignment (VA) mode applications.

4. Conclusions

1*H*,1*H*,2*H*,2*H*-Perfluorodecanethioethermethyl-substituted polystyrenes (PCMSF#) were synthesized to study the effect of the side groups on the liquid crystal (LC) alignment behavior of the LC cells made from these polymer films. Vertical LC alignment behavior with pretilt angles of almost 90° was observed for the LC cells made from the rubbed films of the polymers having higher molar contents of perfluorodecane thioethermethyl side groups. Overall, those side chain groups imparting lower surface energy align the LCs vertically. Critical surface energy values for the formation of the vertical alignment were found to exist. Vertically aligned LC cells could be prepared when the surface energy values of the films were smaller about 8.77 mJ/m^2. The LC cell made from PCMSF100 film exhibited high voltage holding ratio of above 99%. The residual DC voltage of these LC cell was found to be very low, about 10 mV. These results provide the fundamental information required for the design of polymer alignment layers for flexible LC devices using vertically aligned LCs.

Acknowledgment

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