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Liquid Crystal Alignment Behavior on Sulfonated Poly(arylene ether sulfone) Films

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A series of sulfonated poly(arylene ether sulfone) (PAES#, # is the feed monomer ratio of 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone) derivatives were synthesized *via* nucleophilic addition to investigate liquid crystal (LC) alignment property of these polymer films. These polymer films exhibited good optical transparency in the visible light region (400-700 nm). For example, transmittance value (about 96 %) of the PAES# film onto glass substrate at 550 nm is better than that (about 90 %) of the polyimide film, the most commonly used LC alignment layers. The LC cells made from the rubbed PAES# films showed the homogeneous planar LC alignment with parallel direction with respect to the rubbing direction. The LC cells having pretilt angles from approximately 3° for twisted nematic (TN) to 0° for planar switching mode were obtained from these PAES# films having molar contents of sulfonate groups in the ranges of 0 to 70 mole %, respectively. The electro-optical characteristics of the LC cells fabricated with the PAES# films such as applying voltage and response time were as good as those fabricated from rubbed polyimide films. We also found that the LC cells made from PAES# films exhibited good thermal stability.

Introduction

Polyimide (PI) has been primarily studied as a polymeric liquid crystal (LC) alignment material.[1] Mechanical rubbing of polyimide (PI) surfaces, commonly and widely used in liquid crystal display (LCD) industry, can produce homogeneous planar LC alignment layers where the LCs are aligned parallel with respect to the rubbing direction on these surfaces,[2] by combination of two factors, geometric restrictions between micro/nano-scale grooves on the surfaces and LC molecules and physico-chemical interaction at the interface between oriented polymer chains on the alignment layer surfaces and LC molecules.[2] This planar LC alignment has superior thermal and long-term stability as well as a strong azimuthal anchoring energy (> 10^{-5} J/m^2).[3] However, polyimide has too high processing temperature (> 200 °C) to make from polyamic acid to polyimide to apply the LC alignment layers for flexible displays based on the plastic substrates. In addition, generally, polyimides have intrisically yellowish coloration problem related to the extent of diimide fragment conjugation.[4] Moreover, the pretilt angle of LC molecules, required for obtaining a defect-free alignment and improving the electro-optical performance, on the polyimide layer surfaces cannot be easily controlled using the rubbing technique by controlling the rubbing condition such as rubbing depth and/or number of rubbings.

Poly(arylene ether sulfone) (PAES) and its derivatives synthesized by the step-growth polymerization of dihydroxy and dihalo monomers, one of the engineering thermoplastics, are widely used in the electronic field due to their high thermal stability, excellent mechanical and electrical properties, as well as their resistance to thermo-oxidation and hydrolysis by acids and bases.[5-10]

In this paper, the LC alignment behavior of the LC cells produced using the PAES films with various degree of sulfonation as an alignment layers was systematically studied. Homogeneous planar LC alignment layers having in the range of approximately 3° for twisted nematic (TN) – 0° for planar switching mode were produced from the LC cell through a rubbing process. The optical transparency of the PAES films and thermal stability of the PAES LC cell are better than those of the widely used polyimide as a LC alignment layer, respectively. The electro-optical (E-O) characteristics of the LC cells fabricated with the polymer films are also included. To the best of our knowledge, it is the first time to report the LC alignment behavior on the PAES films for display applications systematically.

Experimental

Materials

3,3'-Disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS) was synthesized from 4,4'-Dichlorodiphenylsulfone (DCDPS, 98.0%, Aldrich) according to the procedure reported by Ueda et al.[11] The yield of SDCDPS after recrystallization from a mixture of *iso*-propyl alcohol and deionized water (7/3, v/v) was 88%. DCDPS and 4,4'-dihydroxybiphenyl (BP, 97.0%, Aldrich) were recrystallized from toluene and methanol, respectively, prior to use. Fuming sulfuric acid (65% SO_3, Merck), sodium hydroxide (NaOH, 98.0%, Daejung), and sodium chloride (NaCl, 99.5%, Daejung) were used as received. Toluene (99.5%, Junsei) was refluxed over calcium hydride and distilled. *N*'-Methyl-2-pyrrolidone (NMP, 99.0%, Junsei), *N*,*N*'-dimethylacetamide (DMAc, 99.0%, Junsei) and *N*,*N*'-dimethylformamide (DMF, 99.0%, Junsei) were stored over molecular sieves under nitrogen. Potassium carbonate (K_2CO_3, 99.0+%, Aldrich) was dried under vacuum prior to use.

Synthesis of Poly(arylene ether sulfone) (PAES#)

Poly(arylene ether sulfone)s (PAES#s) were synthesized by the step-growth polymerization between the 4,4'-dihydroxybiphenyl (BP) and two kinds of dichloro monomers such as 3,3'-disulfonate-4,4'-

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dichlorodiphenylsulfone (SDCDPS) and 4,4'-dichlorodiphenylsulfone (DCDPS).[12] When the molar ratios of SDCDPS to DCDPS were 0:100, 25:75, 50:50, 70:30, and 90:10, they are represented by PAES0, PAES25, PAES50 PAES70, and PAES90, respectively. The following procedure was used for the preparation of PAES50. A 250 mL three-neck round bottom flask equipped with a mechanical stirrer, a Dean-Stark trap, a condenser, and a nitrogen inlet and outlet was charged with 5.00 g (26.9 mmol) of BP, 6.60 g (13.4 mmol) of SDCDPS, 3.86 g (13.4 mmol) of DCDPS, 4.27 g (30.9 mmol) of K_2CO_3 in 45.2 mL of NMP (~25 wt. %). Then 22.6 mL of toluene (NMP/toluene = 2/1 v/v) was added as an azeotroping agent. The mixed solution was heated at 145 ^oC for 4 h to ensure complete dehydration and then the temperature was raised slowly to 190 ^oC for the complete removal of the toluene. The reaction was continued for 12-36 h when the solution became very viscous. After the solution was cooled to room temperature, 10.0 mL of NMP was added to dilute the solution. The homogeneous solution was filtered to remove the salts and poured into *iso*-propyl alcohol (1000 mL) to precipitate the polymer, and then the precipitate was rinsed several times with *iso*-propyl alcohol. Product polymer was obtained in 92% of yield after being dried in a vacuum oven for 12 h. PAES0, PAES25, PAES70, and PAES90 were prepared using the same procedure except the molar ratio of SDCDPS to DCDPS and polymerization temperature. The polymerization temperature of PAES0 (Yield > 95%), PAES25 (Yield > 95%), PAES70 (Yield > 90%), and PAES90 (Yield > 80%) were 160, 180, 190, and 190 ^oC, respectively.

Film Preparation and LC Cell Assembly

The PAES# solution (2 wt%) in DMF was prepared. These solutions were filtered through a polytetrafluoroethylene (PTFE) membrane with a pore size of 0.45 μm. Thin films of the polymers were prepared by spin-coating (2000 rpm, 60 sec) them onto 2 × 2 cm^2 indium tin oxide (ITO) coated glass substrates. The films were baked at 150 ^oC for 30 min. Polyimide resin (RN-1175) was dissolved in varnish as supplied by the manufacturer to prepare 4 wt. % polymer solutions. The alignment agents were spin coated (1800 rpm, 9 sec) 2 × 2 cm^2 ITO coated glass substrates. The films were prebaked at 80 ^oC for 30 min and then were fully baked at 200 ^oC for 50 min. These polymer films were rubbed using a rubbing machine (RMS-50-M, Nam Il Optical Components Corp.). Twisted nematic (TN) and antiparallel LC cells were fabricated using the rubbed polymer films onto the ITO coated glass slides. The TN and antiparallel LC cells were made by assembling the films together orthogonally and antiparallel with respect to the rubbing direction for the rubbed polymer films using spacers with a thickness of 4.5 μm, respectively. The fabricated LC cells were filled with a nematic LC, 4-*n*-pentyl-4'-cyanobiphenyl (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), in the isotropic state in order to avoid creating flow alignment by capillary action. The manufactured LC cells were sealed with epoxy.

Instrumentation

The ^1H NMR spectra was collected on Avance 400 (Bruker, Germany) with a proton frequency of 400 MHz. During the experiments, dimethyl-d_6 sulfoxide (DMSO-d_6) was used as the solvent and tetramethylsilane (TMS) was used as the internal standard. FT-IR spectra of samples were recorded in the attenuated total reflectance (ATR) mode in the frequency range of 4000 to 650 cm^{-1} on a Nicolet 6700 instrument (Thermo Scientific, USA). The spectra were recorded as the average of 32 scans with the resolution of 4 cm^{-1}. The samples were put in equal physical contact with the sampling plate of the spectrometer accessory to avoid differences caused by pressure and penetration depth. Molecular weights (M_w, M_n) were measured at 35 ^oC by gel permeation chromatography (GPC) consisting of a Waters 510 HPLC pump, three columns PLgel 5 μm guard, MIXED-C, MIXED-D, and a Viscoter T60A dual detector. HPLC grade DMF was used as eluent and the flow rate was 1.0 mL min^{-1}. Calibration was performed with poly(methyl methacrylate) standards. Thermogravimetric analysis (TGA) was carried out using Q-5000IR (TA instruments, USA) under nitrogen atmosphere in the temperature range from 80 to 800 ^oC at a heating rate of 10 ^oC min^{-1}. The samples were pre-heated at 120 ^oC for 15 min to remove the absorbed moisture before each test. The optical transmittance of the polymer films was obtained using UV-Vis spectroscopy (Perkin Elmer Lamda 20 spectrometer). For the UV-Vis spectroscopy of polymer, the polymer films were prepared by spin-coating PAES# in DMF onto ITO coated glass substrates at 2000 rpm for 60 sec. 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, Aldrich) was dissolved at 1 wt% in 5CB using an optical apparatus equipped with a He-Ne laser, a polarizer, and a photodiode detector as a function of rotation angle of samples.[3] The cell gap was measured before filling the LCs using a spectrophotometer (Ocean optics Inc., S 2000). The pretilt angle of the antiparallel LC cell was measured by the crystal rotation method.[13] The azimuthal anchoring energy of the LC cells was calculated using a torque balance equation written as

$$E_{\varphi} = K_{22}\,\frac{2\times(\Phi-\Delta\varphi)}{d_e\,\sin(\Phi-\Delta\varphi)}$$

where K_{22} is the elastic constant of liquid crystal, the d_e is the cell gap measured using the spectrophotometer, Φ is the intended twist angle and $\Delta\varphi$ the is actual twist angle. The polarized optical microscopy (POM) images of the LC cells were observed using an optical microscopy (Nikon, ECLIPSE E600 POL) equipped with a polarizer and digital camera (Nikon, COOLPIX995). The response time and voltage-transmittance (V-T) were measured from the LC cells using the same method as that reported by others.[14,15] The threshold voltage (V_{th}) and driving voltage (V_{on}) in the V-T curve are defined as the voltages at which the transmittance was decreased to 90 % and 10 % of the initial transmittance value, respectively. The rising (T_r) and falling (T_f) response times for the white-to-black and black-to-white changes, respectively, are defined as the time to transition from 10 to 90 % transmittance and vice versa.[14,15]

Results and Discussion

A series of poly(arylene ether sulfone)s (PAES#) were synthesized *via* nucleophilic aromatic substitution polycondensation of 4,4'-dihydroxybiphenyl (BP), 4,4'-dichlorodiphenylsulfone (DCDPS) and 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone (SDCDPS), as shown in Fig. 1. In the preparation of the sulfonated PAES copolymers from PAES25 to PAES90, the higher polymerization temperature was needed than that of non-sulfonated PAES, PAES0, to sufficiently facilitate the nucleophilic substitution reaction of the sterically hindered SDCDPS monomer.[16] Careful dehydration of the monomer mixtures and complete removal of the toluene are also required to obtain high molecular weight PAES copolymers. Typical weight-average molecular weights (M_w)s and M_w/M_ns of the PAES copolymers calculated from the GPC measurement range from 48,300 to 96,000 and 1.76 to 2.89, respectively (Table 1). All the weight average molecular weights were indicative of good film forming characteristics.

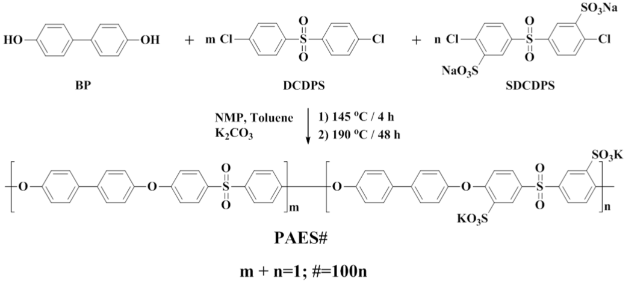

Fig. 1 Synthesis of poly(arylene ether sulfone)s (PAES#)s.

Table 1 Synthesis and properties of PAES#

Polymer	M_w[a] (g mol^{-1})	M_n[a] (g mol^{-1})	Degree of sulfonation (mol%) Feed[b]	Degree of sulfonation (mol%) In polymer[c]	T_{d10}[d] (°C)	Char yield at 800 °C (%)	Pretilt angle (°C)[e]	Water Contact angle (°C)[f]
PAES0	90,600	48,200	0	0	535	38	3	82
PAES25	96,000	54,700	25	23	520	56	2.7	70
PAES50	85,000	29,400	50	47	520	57	0.9	57
PAES70	81,100	35,100	70	67	519	58	0.5	49
PAES90	48,300	24,400	90	85	519	60	0	—[g]

[a] Weight-average molecular weight (M_w) and number average molecular weight (M_n) were calculated from the result of GPC measurement using polymethyl methacrylate standards samples.

[b] Degree of sulfonation calculated from feed monomer ratio.

[c] Degree of sulfonation calculated from peak integration in ^{1}H NMR spectrum.

[d] The 5% weight loss temperature from the initial weight by TGA measurement under N_2.

[e] Measured using crystal rotation method.

[f] Measured from static contact angles.

[g] Not measurable due to the water soluble characteristics.

The chemical structures and compositions of the obtained copolymers were confirmed by ^{1}H NMR spectroscopy. Fig. 2 shows the ^{1}H NMR spectrum for the PAES50 as a representative ^{1}H NMR spectra of the other PAES copolymers. Since the feed molar ratio of SDCDPS and DCDPS is 1:1, degree of sulfonation (DS) of 50 mol% was expected. The DS of PAES50 calculated from the peak integration of ^{1}H NMR spectrum was 47 mol%. Possibly slightly different reactivity between SDCDPS and DCDPS caused this result as reported by us and others.[16-18] Similar integrations and calculations for PAES25, PAES70 and PAES90 were performed and were typically within ± 5% of the expected values from the synthesis (Table 1).

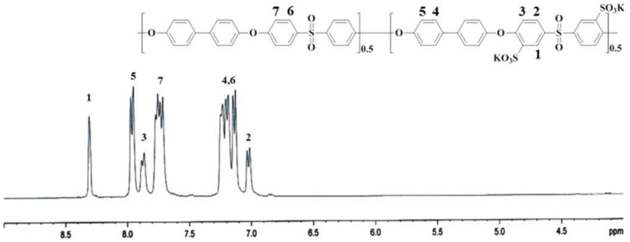

Fig. 2 ^{1}H NMR spectrum of PAES50.

The successful introduction of the sulfonate groups on the PAES# was also confirmed by FT-IR spectra (Fig. 3). The characteristic peaks at 1030, 1098 and 1470 cm^{-1} assigned to symmetric and asymmetric stretching of the sulfonate groups were observed for all sulfonated PAES copolymers from PAES25 to PAES90.[11] The intensity of these peaks increased with an increase in the DS. From the GPC, ^{1}H NMR, FT-IR measurements, it could be concluded that the high molecular weight PAES copolymers with various DS were successfully synthesized.

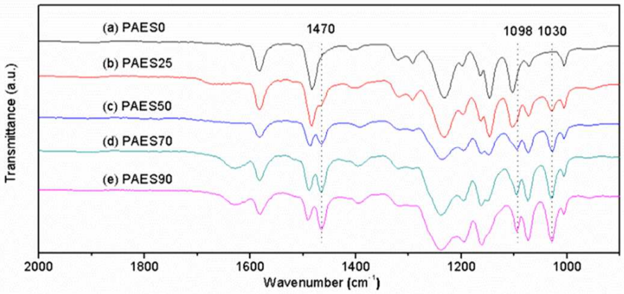

Fig. 3 Infrared spectra of (a) PAES0, (b) PAES25, (c) PAES50, (d) PAES70, and (e) PAES90.

The thermal behaviors of the PAES copolymers were investigated by TGA under nitrogen atmosphere, as shown in Fig. 4. All the samples were pre-heated at 120 °C for 15 min in the TGA furnace to remove the absorbed moisture. The influence of the DS on both degradation temperature (T_{d10}, 10 wt. % of weight loss from the initial weight) and the residual char yield (%) at 800 °C are also summarized in Table 1. PAES0 is well known to be a thermally stable polymer and showed a T_{d10} at 535 °C. The T_{d10}s for the sulfonated PAES copolymers from PAES25 to PAES90 were lower than that of the PAES0. However, the char yield at 800 °C showed a reverse trend. The char yield for the sulfonated PAES copolymers increased slightly with an increase in the DS. The high char yields of the sulfonated PAES copolymers correlate well with the findings of Robeson and Matzner, confirming the utility of SDCDPS as a flame retardant additive in polyarylate blends.[19] Among the series of synthesized polymers, PAES0, PAES25, PAES50, and PAES70 are chosen as alignment layer coating materials, as PAES90 is soluble in water. Since these polymers are soluble in aprotic polar solvents, such as DMF, NMP, and DMAc, thin films of the polymers onto glass substrates were prepared by spin-coating them using DMF.

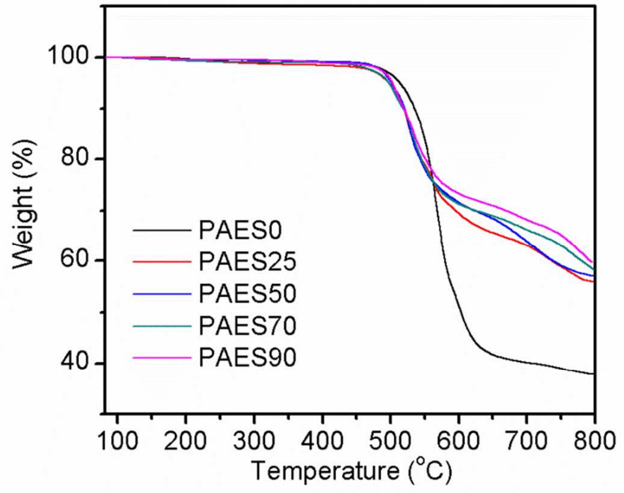

Fig. 4 TGA spectra of PAES#.

Quantitative analysis of transparency of PAES# films was evaluated using UV-Vis spectra to investigate the possibility for the surface coating applications (Fig. 5). At first, the transmittance value of the coated PAES# film onto glass substrate is about 96 % at 550 nm. This value is lower than that of the bare glass substrate, even that (90 %) of the widely used polyimide film having intrisical yellowish coloration problem related to the diimide fragment conjugation as a LC alignment layer.[4] Conclusively, the optical transparency of the PAES# film in the visible light region is good enough to be used as optical materials for display devices.

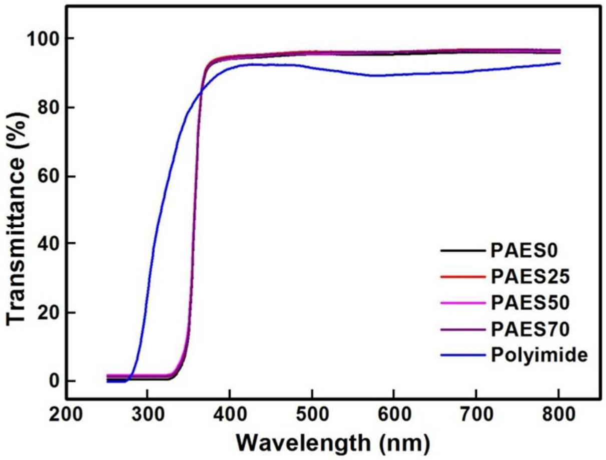

Fig. 5 UV-Vis transmittance spectra of poly(arylene ether sulfone) derivatives and polyimide alignment layers onto quartz substrates.

The LC alignment behavior of the LC cells fabricated with the rubbed PAES# films was investigated using polarized optical microscopy (POM). The orthoscopic and conoscopic POM images of the LC cells made from rubbed PAES# films clearly show homogeneous planar LC alignment behavior (Fig. 6). We found that the aligning ability of the LC cells made from the rubbed PAES# films exhibited similar LC alignment behavior compared with the LC cells fabricated with rubbed polyimide films by POM image as well as LC cell image by naked eyes under crossed polarizers. The LC (5CB) molecules used in this study are composed of biphenyl group and polar terminal groups such as cyano group. We believe that 5CB molecules interact anisotropically with the oriented biphenyl and sulfone and sulfonate moiety on the PAES# films *via* π-π and/or dipole-dipole and/or van der Waals interaction. Anchoring energy values of the LC cell fabricated with rubbed PAES# film are above the level of ~ 10^{-5} J/m^2. These values are comparable with those of conventional polyimide (from ~ 10^{-5} to ~ 10^{-3} J/m^2) in the LCD industry, as previously reported.[3] The LC cells fabricated from the rubbed PAES# films have maintained a homogeneous alignment of the LC for more than several months since we first made the LC cell.

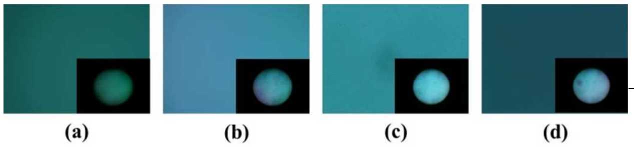

Fig. 6 Orthoscopic and conoscopic POM images of the LC cells made from rubbed PAES# ((a) PAES0, (b) PAES25, (c) PAES50, and (d) PAES70) films.

Polar diagrams of the absorbance of the dichroic dye (disperse blue 1) in the antiparallel LC cells fabricated using the rubbed PAES# films were obtained in order to investigate the effect of rubbing on the LC alignment direction accurately (Fig. 7). As expected, the maximum absorbance along the $0^o \leftrightarrow 180^o$ direction was observed after the rubbing process indicating the LC cells fabricated with all PAES# films have parallel LC alignment with respect to the rubbing direction, as in the case of the LC cell made from rubbed polyimide film as reported by others.[3]

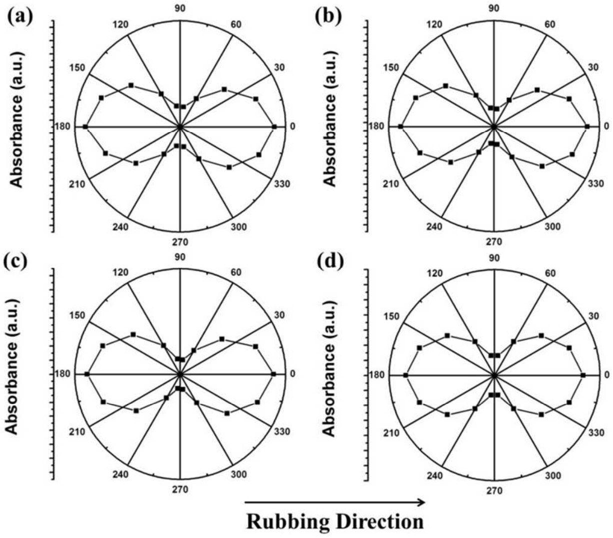

Fig. 7 Polar diagrams of the absorbance of a dichroic dye (disperse blue 1) in the antiparallel LC cells fabricated using the PAES# ((a) PAES0, (b) PAES25, (c) PAES50, and (d) PAES70) films as a function of rotation angle of the samples.

The pretilt angles of the antiparallel LC cells fabricated with the polymer films were measured, in order to determine the effect of the DS on the LC alignment direction (Table 1). As the molar content of the sulfonate groups in the PAES# increases from 0 to 70 mol%, the pretilt angle of the LC decreases from approximately 3^o for twisted nematic (TN) to 0^o for planar switching mode. The water contact angles on the polymer films were measured in order to investigate the effect of wettability on the pretilt angle of LCs (Table 1). The water contact angles on the polymer films were determined in static mode. The water contact angles on the polymer films decreased with an increase in the DS, indicating that the changes in pretilt angle are related to the changes in wettability on the polymer films, as described previously.[20-22]

The electro-optical performance of the LC cells having the same cell gap of about 4.5 µm was determined by measuring the voltage-transmittance (V-T) and response time values using the same conditions. The V-T curves were almost identical for the two alignment films when 10 V was applied to each cell. The V_{th}, V_{50}, and response time of the rubbed PAES50 film were 1.18 V, 1.60 V, and 65 ms, respectively, which are close to those of rubbed polyimide in the LCD industry, 1.10 V, 1.35 V, and 40 ms, respectively (Table 2).

Table 2 Voltage-transmittance and response time value of the LC cell made from polymer film

Sample	Voltage–transmittance (V)			Response time (ms)		
	V_{th}	V_{50}	V_{on}	T_r	T_f	T_t
PAES50	1.18	1.60	1.98	24	41	65
Polyimide	1.10	1.35	1.72	15	25	40

The thermal stability of the LC cells made from the rubbed PAES# films was measured to investigate the optical stability of the polymer film by heating to the various temperatures for 2 h. The LC cells prepared from all PAES# film heated to 250 ^{o}C for 2 h exhibit the planar LC alignment behavior without any partial defects (Fig. 8). Therefore, the thermal stability of the LC cell made from PAES# film is similar with that of the polyimide film.

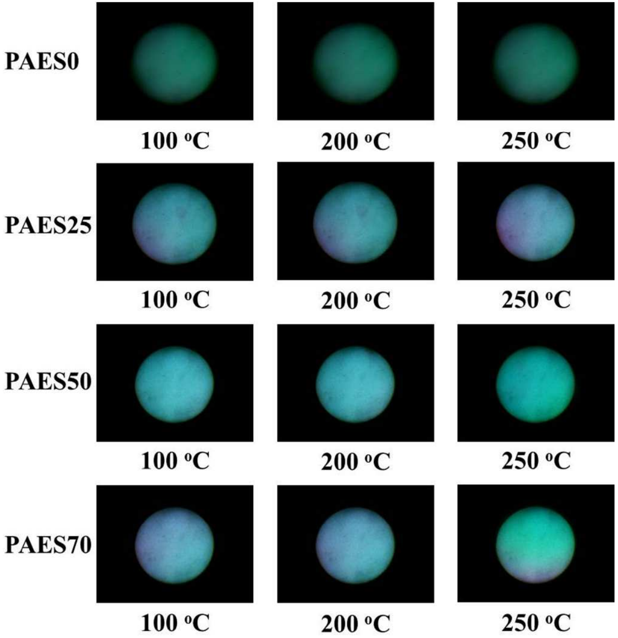

Fig. 8 (a) Concoscopic POM images of the LC cells made rubbed PAES# films, after thermal treatment at 100, 200, and 250 ^{o}C for 2 h, respectively.

Conclusions

The LC cell prepared using the PAES# as the alignment layer showed the homogeneous and planar LC alignment behavior. The superior optical transparency of the PAES# films compared with polyimide film was observed in the visible light region. As the molar content of the sulfonate groups in the PAES# increases from 0 to 70 mol%, the pretilt angle of the LC decreases from approximately 3^{o} for twisted nematic (TN) to 0^{o} for planar switching mode. Good electro-optical (E-O) properties were observed for the LC cells made from the PAES# film. For example, V_{th}, V_{50}, and response time of the rubbed PAES50 film were 1.18 V, 1.60 V, and 65 ms, respectively, which are close to those of rubbed polyimide in the LCD industry, 1.10 V, 1.35 V, and 40 ms, respectively, indicating that these LC cells can be used for practical LC display applications, because they have a high thermal stability. Therefore it was firstly found that the sulfonated poly(arylene ether sulfone)-based materials can produce a LC alignment system.

Acknowledgements

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