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Influence of molecular mass on the liquid crystal alignment of photosensitive fluorinated polyester films

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Photosensitive fluorinated polyesters (polymer-*n*) of varying molecular mass M_n (number-average molecular mass) were synthesized. The thin films formed from polymer-*n* samples could induce liquid crystal (LC) alignment after irradiation by linearly polarized ultraviolet light. The LC alignment direction on the irradiated films was investigated in detail by linearly polarized infrared spectroscopy and polarizing optical microscopy. It was found that LC alignment behaviour changed with change in the molecular mass of polymer-*n*: irradiated films with lower or higher M_n induced homeotropic or homogenous alignment, respectively. There was no clear morphological anisotropy in these aligned films, as observed by atomic force microscopy. The surface energies of the irradiated films were also measured using the indirect contact angle method, where both surface energy and its polar component increased with increasing M_n. The variation in M_n could be considered as a main reason for varying alignment behaviour.

1. Introduction

In recent years, liquid crystal (LC) photoalignment technique has attracted considerable attention in the field of optical and electronic devices, because it avoids some drawbacks of the traditional rubbing method for LC alignment, such as sample contamination, static charge generation, and scratching [1–4]. Moreover, the photoalignment technique can be used not only to control LC alignment in a certain direction, but also to fabricate multi-domains to overcome the intrinsic viewing angle problem in LC display devices. Several kinds of photosensitive material have been studied in detail for the photoalignment layer, including poly(vinyl cinnamate) [1], coumarin [2], azobenzene-containing polymers [3] and other derivatives [4].

Poly(vinyl cinnamate), a polymer containing cinnamate side groups, shows a complex alignment behaviour that results from the competition between *E*/*Z* photoisomerization and [2+2] photocycloaddition. The photoalignment resulting from *E*/*Z* photoisomerization is unstable due to the reversible isomerization reaction [5]. However, [2+2] photocycloaddition reactions result in a stabilization of the induced structure due to photocrosslinking, which leads to higher temperature and solvent stability of the irradiated films [1, 6]. Song *et al.* [7] reported that PDA-*n* polyesters have photoreactive sites in the polymer main chain but not in the side chain, which is different from poly(vinyl cinnamate). Li *et al.* [8] prepared a LC photoalignment material containing photosensitive main chains, and validated that [2+2] cycloaddition between the chalcone moieties generated a surface anisotropy, which induced efficient LC alignment. The material was thermally stable up to 344°C in a nitrogen atmosphere. There are, however, few reports regarding the effect of molecular mass on LC alignment by a polyester with photoreactive main chain.

Molecular mass is also an important parameter of a polymer, which can affect many of its characteristics, such as transition temperature, viscosity and equilibrium morphology of a LC alignment film [9]. In this paper we report the effect of molecular mass on alignment by a polyester with photosensitive main chain; chemical structure of this polymer, poly[5-(3,5-bistrifluoromethylphenyloxycarbonyl)-1,3-diphenyloxy-1,4-phenylenediacryloyl] (polymer-*n* II), is given in scheme 1. It was found that photoalignment films of polymer-*n* with lower or higher molecular mass would induce homeotropic or homogeneous LC alignment, respectively. The effect of the molecular mass of polymer-*n* on the mechanism of LC alignment of a thin film formed from the polymers was also examined.

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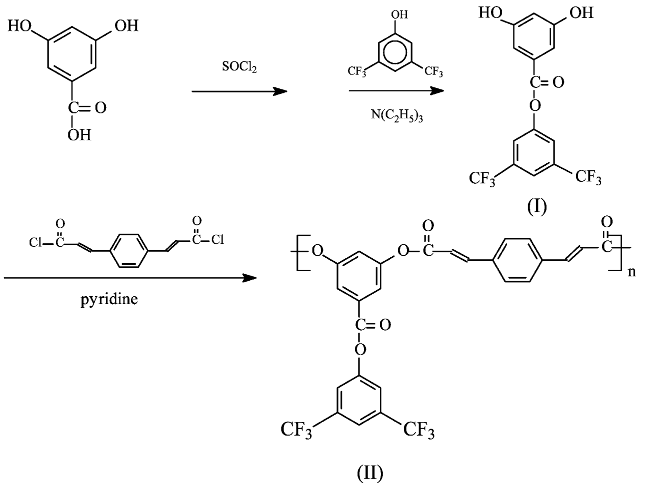

Scheme 1. Method of preparation of poly[5-(3,5-bistrifluoromethylphenyloxycarbonyl)-1,3-diphenyloxy-1,4-phenylenediacryloyl] (polymer-*n*).

2. Experimental

2.1. *Materials and synthesis*

3,5-Dihydroxybenzoic acid and 3,5-bis(trifluoromethyl)phenol were purchased from Aldrich. 1,4-Phenylenediacrylic acid dichloride was prepared as described in [10]. *N*,*N*-dimethylformamide (DMF) was stirred with $MgSO_4$ overnight and distilled under reduced pressure. Tetrahydrofuran (THF) was dried over sodium metal and distilled under a nitrogen atmosphere. Other chemicals and solvents were obtained from Shanghai Chemical Inc. and directly used without further purification. The synthetic routes of the monomer and polymer are shown in scheme 1.

2.1.1. 5-[3,5-Bis(trifluoromethyl)phenyloxycarbonyl]-1,3-dimethylphenoxide (I). 3,5-Dihydroxybenzoic acid (0.02 mol) and thionyl chloride (0.022 mol) were dissolved in THF (100 ml). A few drops of DMF were added as catalyst and the mixture was heated reflux under N_2 at 50°C for 4 h. Surplus thionyl chloride was removed under reduced pressure and the obtained solution (**1**) was then cooled to room temperature for use in the next stage.

3,5-Bis(trifluoromethyl)phenol (0.02 mol) and pyridine (3.5 g) were dissolved in THF (100 ml). The solution was cooled to 0°C with stirring and solution (1) was added over a 0.5 h period under N_2. The resulting mixture (2) was stirred at 0°C for 3 h, then poured into water to precipitate product (I) 86% yield. Product (I) was characterized by FTIR spectroscopy. FTIR (powder, KBr, cm^{-1}): 1179 (C–O, ν), 1279 ($-CF_3$, ν), 1613 (C=C, phenyl group, ν), 1741 (C=O, ν), 3200–3450 (–OH, ν).

2.1.2. Poly[5-(3,5-bistrifluoromethylphenyloxycarbonyl)-1,3-diphenyloxy-1,4-phenylenediacryloyl] (II): polymer-*n* (*n*=1, 2, 3). A mixture of 5-(trifluoromethyl)-1,3-phenylenediamine (0.022 mol) and pyridine (3.5 g) in THF (100 ml) was stirred at 0°C. 1,4-Phenylenediacrylic acid dichloride (0.02 mol) in THF (100 ml) was added over a 0.5 h period under N_2. The mixture was then stirred for 4 h and filtered. The solution was poured into water and the product polymer-1 was precipitated. The insoluble yellow product was washed with 0.01M HC1, 0.01M Na_2CO_3 solution and water. After drying, the product was divided into two components by treatment with DMF: the soluble component was polymer-2; the insoluble component was polymer-3. All the products were dried under vacuum and the yields of polymer-1,2,3 were 30%, 20% and 35%, respectively. The three products had the same IR spectra. FTIR (powder, KBr, cm^{-1}): 975 (=CH, δ), 1181 (C–O, ν), 1283 ($-CF_3$, ν), 1629 (C=C, phenyl group, ν), 1724 (C=O, ν), 3075 (–CH, ν).

2.2. *Preparation of irradiated films and LC cells*

Polymer-*n* (*n*=1, 2, 3) were dissolved in THF, DMF and NMP, respectively, to give 1 wt% solution. Each polymer solution was spin-coated onto calcium fluoride windows for polarized FTIR spectra, and onto indium tin oxide glass substrates for AFM measurements, surface energy calculation and LC cell assembly. The coated films were immediately irradiated by linearly polarized ultraviolet light (LPUVL) from a 300 W Hg–Xe lamp with a Glan–Thomson prism at room temperature. A 280 nm filter (Model 58600 Oriel) was used to obtain the desired UV wavelength. The incident light was perpendicular to the film surface with an intensity of 1.0 mW cm^{-2}. All the polymer films were irradiated under the LPUVL at 0.9 J cm^{-2}, to give uniform and stable LC alignment in the experiments.

Parallel LC cells were fabricated with the irradiated polymer-coated substrates, with cell gaps of approximately 40 μm. The commercial LC material 5CB (T_{NI}=35.4°C, Aldrich) was injected into the cells at 36°C. The cells were then cooled to room temperature at which 5CB exhibited the nematic phase.

2.3. *Characterization*

Gel permeation chromatography (GPC, Waters 410) was used to obtain the equivalent molecular masses of the polymer-*n*. To reveal the LC alignment of the polymers, polarized FTIR spectra were recorded on a BIO-RAD FTS-3000 spectrophotometer equipped with an IR polarizer (Graseby Specac, UK). Spectra in the mid-infrared region (4000–1000 cm^{-1}) were collected with 30 co-addition scans at a spectral resolution of $2\,\mathrm{cm}^{-1}$. LC alignment behaviour was also evaluated by polarizing optical microscope. Conoscope observation with the polarizing microscope was used to estimate homeotropic alignment. AFM (Dimension 3100, Digital Instrument) was used to obtain surface morphologies of the irradiated film, the scan rate was 1.001 Hz.

Surface energies of the irradiated films were calculated from water and glycerol contact angles. Contact angle measurements were performed on a stage equipped with a video camcorder (Contact Angle Analyzer JJC-I, Changchun No.5 Optical Instrument, Ltd). The contact angles were measured after the droplets had been in contact with the surface of the film for 1 min. The polarity and total surface energies were calculated according to the Owens–Wendt–Kaelble–Young equation [11].

3. Results and discussion

3.1. *Molecular masses*

Dried samples of polymer-1 and polymer-2 were dissolved in THF and DMF, respectively. They were then filtered through a 0.45 mm syringe filter before manual injection into a GPC system. The GPC measurements were conducted at 35°C with a flow rate of $1.0\,\mathrm{ml\,min}^{-1}$. The molecular mass and polydispersity of the products were calibrated using polystyrene molecular mass standards [12]; the polymer-*n* equivalent molecular mass are listed in table 1.

3.2. *LC alignment behaviour*

The LC alignment direction was studied using polarized FTIR spectroscopic measurements carried out on a FTIR spectrometer equipped with an IR polarizer. The polarizer and LC cell were placed in the optical path of the IR instrument, and the LC cell planes were installed perpendicular to the incident beam direction. All absorbance intensities were measured at the absorption peak associated with the nitrile group (–C≡N) at $2231\,\mathrm{cm}^{-1}$, which was clearly located in the IR spectra. The IR vibration direction of the nitrile group is considered as the alignment direction of 5CB.

Table 1. Equivalent molecular masses of polymer-*n*.

Material	M_n	M_w	PD[a]
Polymer-1	4840	4901	1.013
Polymer-2	11336	12589	1.293
Polymer-3	>11336		

[a]Polydispersity index.

Figure 1 gives polar diagrams of the peak intensity at $2231\,\mathrm{cm}^{-1}$ of LC molecules with a polymer-*n* alignment film. Figure 1A shows the polarized absorbance of irradiated polymer-1 films from 0° to 360°; the values are almost constant. In this figure, we can assume the alignment is homeotropic. In order further to confirm alignment direction, the polarizing optical microscope was employed. The dark state, when studied with crossed polarizers, did not change on rotation of the sample in the plane of the viewing stage, as shown in figure 2A. This is because the axis of the homeotropically aligned LC molecules is perpendicular to the viewing direction. In addition, a dark crossed brush appeared through conoscopic observation, which is a significant indication for homeotropic alignment, as shown in figure 2A′. Clearly, the irradiated films of polymer-1 induced LC homeotropic alignment. The same results were obtained for polymer-2 (see figures 1B and 2B, 2B′).

In the case of films of polymer-3, as shown in figure 1C, the absorbance of the nitrile group has a maximum intensity along the direction 90°↔270°, which is perpendicular to the electric field vector **E** of the incident LPUVL. This result indicates that LC molecules in contact with the polymer-3 film surface are homogeneously induced to align nearly perpendicular to vector **E**. Photoalignment of the LC was also revealed by polarizing optical micrographs of the LC cell. As shown in figures 2C and 2C′, the bright states of the light through an irradiated cell appear at 45°, 135°, 225° and 315°, with a regular interval of 90°. These results confirm that films of irradiated polymer-3 induced homogeneous LC alignment.

3.3. *Surface morphology*

Figure 3 shows representative AFM images of irradiated polymer-*n* films. Figure 3A is an AFM image of the photoalignment surface of a polymer-1 film with M_n=4 840. Surface profiles were obtained along lines a-1 (perpendicular to the vector **E**) and a-2 (parallel to the vector **E**) as indicated in figure 3A, and the results are shown in figure 3a-1,2. These surface profiles indicate that the root mean square (rms) surface roughness is 1.664 nm across the **E** lines (i.e. along line a-1) and 1.952 nm along the **E** lines (along line a-2). This irradiated film has none of the typical scratch lines often observed for rubbed PI films [13, 14]. No obvious anisotropy was observed in the surface image and the LC alignment direction could not be judged from the surface images. A similar AFM image was obtained for irradiated polymer-2 films with M_n=11 336, as shown in figure 3B. The surface profiles in figure 3b-1,2 indicate that the rms surface roughness of this film is 2.669 nm

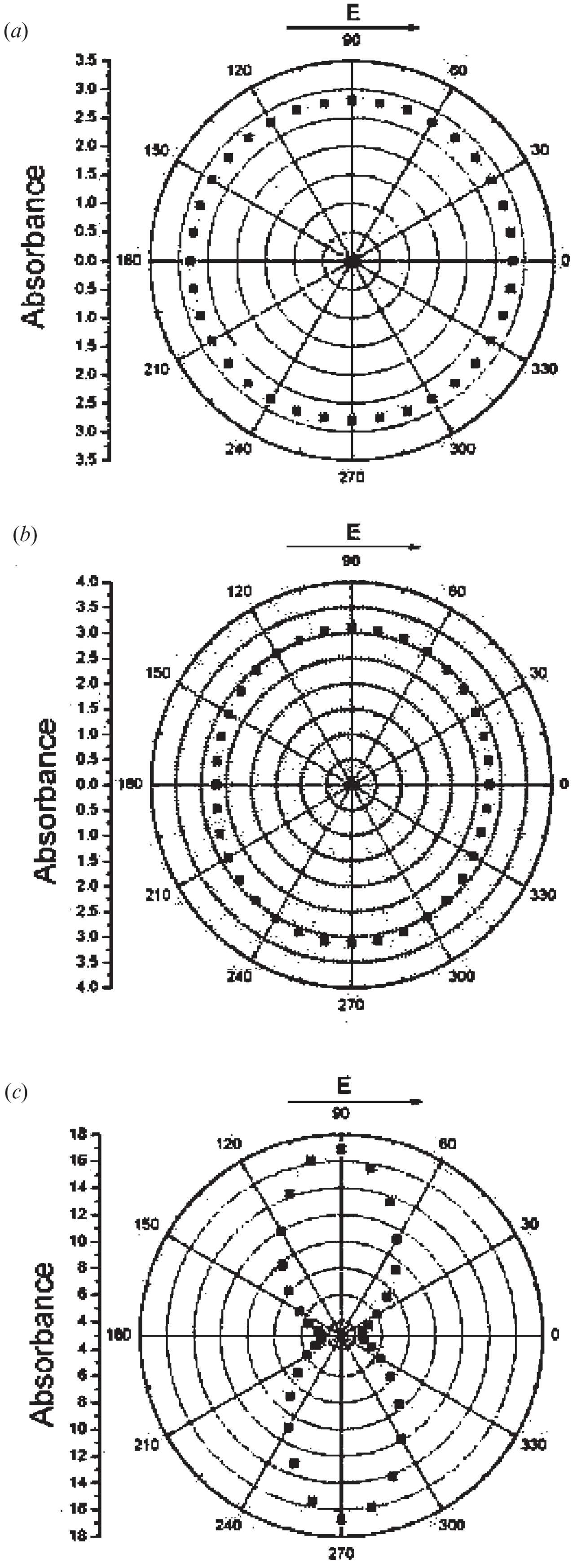

Figure 1. Angular absorbance intensity of IR peak at 2231 cm^{-1} (nitrile group) of LC cells containing 5CB: (A) polymer-1, (B) polymer-2, (C) polymer-3.

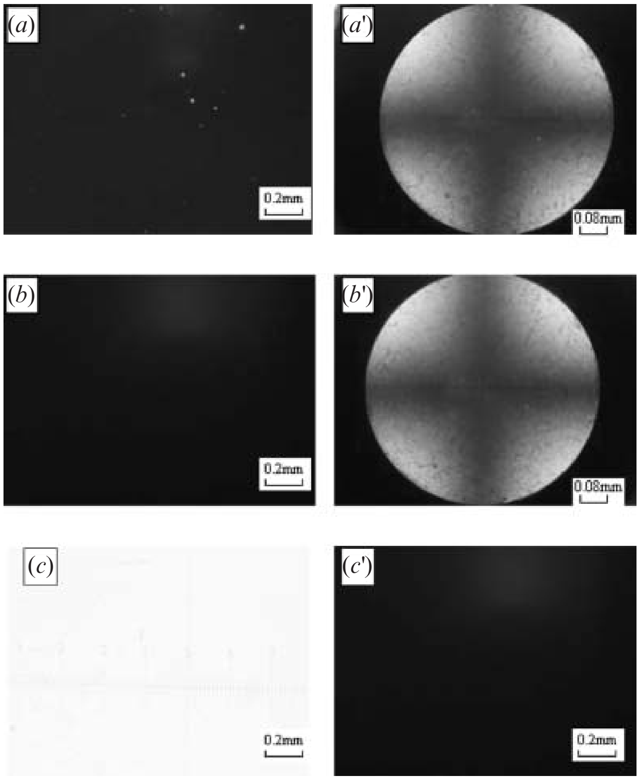

Figure 2. Polarized optical micrographs of LC cells: (A) polymer-1; (A′) polymer-1 (conoscopic observation); (B) polymer-2; (B′) polymer-2 (conoscopic observation); (C) polymer-3 (bright states); (C′) polymer-3 (dark states).

along line b-1 and 2.631 nm along line b-2. The surface roughness of this irradiated polymer-2 film is greater than that observed for the irradiated polymer-1 film.

Polymer-3 with M_n>11 336 shows a smoother surface, see figure 3C. The surface profiles in figure 3c-1,2 indicate a rms surface roughness of 0.263 nm along line c-1 and 0.277 nm along line c-2. The surface roughness of this irradiated polymer-3 film is smaller than those observed for irradiated polymer-1 and polymer-2 films, and no significant topography was observed from the surface morphologies, unlike the two previously mentioned films. Therefore, such a slight roughness of the aligned films should have little influence on the photoalignment behaviour of the films.

3.4. *Surface energy*

To clarify the reason for different LC alignments on irradiated polymer-*n* films, surface energies were measured using the indirect contact angle method, and

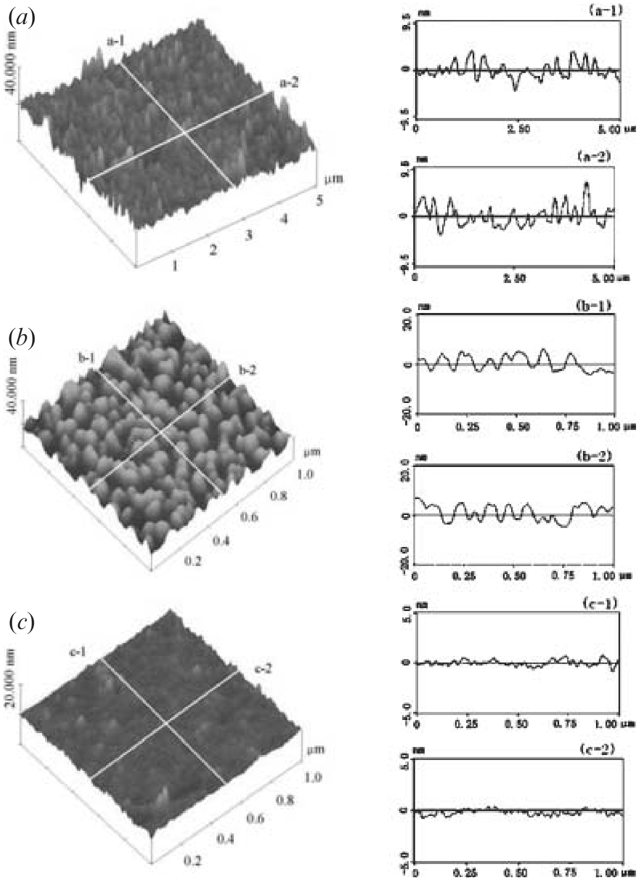

Figure 3. AFM images and surface profiles of polymer films with various molecular masses photoinduced with 0.9 J cm^{-2} of UV radiation: (A, a-1, a-2) 4840; (B, b-1, b-2) 11336; (C, c-1, c-2) >11336.

calculated according to the Owens–Wendt–Kaelble–Young equation:

$$\gamma_{\mathrm{L}}^{\mathrm{t}}(1+\cos\theta)=2\left(\gamma_{\mathrm{L}}^{\mathrm{d}}\gamma_{\mathrm{S}}^{\mathrm{d}}\right)^{1/2}+2\left(\gamma_{\mathrm{L}}^{\mathrm{p}}\gamma_{\mathrm{S}}^{\mathrm{p}}\right)^{1/2}$$

where θ is Young's contact angle, γ^{d} and γ^{p} are, respectively, dispersion and polar components of surface energy noted, such that $\gamma^{\mathrm{t}}=\gamma^{\mathrm{d}}+\gamma^{\mathrm{p}}$. The two liquids used for contact angle measurement were water and glycerol: $\gamma^{d}_{\mathrm{water}}=21.8$, $\gamma^{p}_{\mathrm{water}}=51.0$, $\gamma^{d}_{\mathrm{glycerol}}=37.0$, $\gamma^{p}_{\mathrm{glycerol}}=26.4\,\mathrm{mJ\ m^{-2}}$ [15]. Hence, the total surface energy $\gamma_{\mathrm{S}}^{\mathrm{t}}$ and the polar surface energy $\gamma_{\mathrm{S}}^{\mathrm{p}}$ of the irradiated films can be calculated.

The water and glycerol contact angles were measured using an environmental chamber at 20°C. At least five droplets at different regions of the same piece of film were dispensed for contact angle measurement, and at least two pieces of film were used. Thus, at least 10 contact angles were averaged for each type of film as well as for each liquid. The contact angle and surface energy data of the three films with different testing liquids are listed in table 2.

LC alignment involves complex physicochemical interactions between the LC molecules and the aligning films. From the experimental results mentioned in table 2, it is clear that the surface energy of an irradiated film increases with increasing molecular mass, which is consistent with former results [16]. The lowest molecular mass polymer-1 with $M_{\mathrm{n}}=4\,840$ has the largest contact angle (102°, 91°) and the lowest total surface energy (17.45 mJ m^{-2}). Moreover, the values of $\gamma_{\mathrm{s}}^{\mathrm{p}}=2.18\,\mathrm{mJ\,m^{-2}}$ and $\gamma_{\mathrm{S}}^{\mathrm{p}}/\gamma_{\mathrm{S}}^{\mathrm{t}}=12.3\%$ are also the lowest. Akiyama and Iimura reported that homeotropic LC alignment was caused by weak anchoring [17]. The polar surface energy of the alignment layer is most important for LC alignment and affects the pretilt angle dramatically [12]. As the polar surface energy of the alignment layer decreases, the interaction between LC and alignment film becomes weaker and then the pretilt angle increases. Sung *et al.* [18] and Yu *et al.* [19] reported results similar to ours. Therefore, in the case of polymer-1 irradiated film, we can confirm that weak polar surface energy plays an important role in homeotropic LC alignment.

The same applies to polymer-2 film ($M_{\mathrm{n}}=11\,336$), which also has lower $\gamma_{\mathrm{S}}^{\mathrm{p}}=3.24\,\mathrm{mJ\,m^{-2}}$ and $\gamma_{\mathrm{S}}^{\mathrm{p}}/\gamma_{\mathrm{S}}^{\mathrm{t}}=16.3\%$. The weak interaction between LC and alignment film was the reason for the generation of homeotropic LC alignment. Polymer-3 has the highest surface energy of 67.89 mJ m^{-2}, in which $\gamma_{\mathrm{S}}^{\mathrm{p}}/\gamma_{\mathrm{S}}^{\mathrm{t}}$ is 90.4%. The larger polar surface energy may increase the interaction between LC and alignment film, which pulls back the LC molecules onto the plane of the film. Thus, the LC was aligned homogeneously on the irradiated polymer-3 coated substrate.

Table 2. Surface energies of polymer-*n* irradiated films.

Material	Irradiation energy/J cm^{-2}	θ_{water}/deg	$\theta_{\mathrm{glycerol}}$/deg	$\gamma_{\mathrm{S}}^{\mathrm{t}}$/mJ m^{-2}	$\gamma_{\mathrm{S}}^{\mathrm{p}}$/mJ m^{-2}	$\gamma_{\mathrm{S}}^{\mathrm{p}}/\gamma_{\mathrm{S}}^{\mathrm{t}}$
Polymer-1	0.9	102 ± 1	91 ± 1	17.45	2.18	12.3%
Polymer-2	0.9	97 ± 1	86 ± 1	19.84	3.24	16.3%
Polymer-3	0.9	30 ± 1	41 ± 1	67.89	61.37	90.4%

4. Conclusion

The LC alignment behaviour and surface morphology of photoalignment films of polymer-*n* with various molecular masses were investigated in detail by linearly polarized IR spectroscopy and AFM. The surface energies of nematic LC molecules on the polymer-*n* photoalignment films were also measured.

Polymer-*n* photoalignment films exhibit LC alignment directions that are significantly dependent on molecular mass: the photoalignment film of polymer-3 with M_n>11336 was a homogeneous alignment film, while films of polymer-1 and polymer-2 with smaller molecules gave homeotropic alignment film. However, the surface morphology of polymer-*n* films is independent of the molecular mass: all the surfaces are smooth and there was no clear morphological anisotropy on these aligned films, as observed through AFM analysis.

On the polymer-*n* film surfaces, LCs were found to anchor with a low anchoring energy, ranging from 17.45 to 67.89 mJ m^{-2}, depending on the molecular mass. Polymer-1 and polymer-2 with lower molecular mass have lower surface and polar energyies, which were the cause of homeotropic alignment films; while for polymer-3, the surface and polar surface energies were larger than those of polymer-1 and polymer-2, resulting in homogenous LC alignment.

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