

Structure and Chain Orientation in Thin Films of Side-Chain Liquid Crystalline Polymers

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With the aim of investigating the effect of the side-chain length on the order and structure of thin films of side-chain liquid crystalline polymers, poly(oxyethylene)s containing various lengths of *n*-alkylsulfonylmethyl side chains ($\text{CH}_2\text{SO}_2(\text{CH}_2)_{m-1}\text{CH}_3$; $m = 5, 7, 10, \text{ and } 16$) were synthesized. The inner structure, surface structure, and adhesion behavior of thin films of these polymers were investigated. An X-ray reflectivity study of a polymer film spin-coated onto a silicon wafer showed that upon annealing above the glass transition temperature, the film has a lamellar structure in which the ordered layers are parallel to the substrate surface. When alkyl chain length in the side group is longer than the critical length, the layered structure is less perfect. Also, the air–polymer surface and the interface between layers are not smooth. This result implies that side chains are presumably loosely oriented. It can be expected that the critical length of the side chain is between $m = 11$ and $m = 16$. Near-edge X-ray absorption fine structure spectroscopy results also confirm that side chains near the top surface are loosely oriented when m is larger than the critical value. Force–displacement curves measured with atomic force microscopy also show an abrupt change in the adhesion force when the alkyl side chain length in the side group is longer than the critical length, which results from the side-chain conformation.

Introduction

The properties of thermotropic liquid crystalline polymers have been the subject of increasing scientific interest.^{1–4} However, most works on liquid crystalline polymers have been concerned with bulk properties, but less work was done on thin films of such materials.^{5–7} Thin films of these materials are widely used in electrical and optical devices, and it is important to investigate the structure and surface properties of these films. The structure of the polymer in thin films could be different from that of bulk material because the molecular configuration and the structural order may be affected by both the substrate–polymer interface and the polymer–air interface.

Generally, polymers containing *n*-alkyl side chains can form mesophases through side-chain crystallization when the side-chain length is longer than the critical value.^{8–12}

Kaufman et al. initially showed that long *n*-alkyl side chains of polymers can pack into paraffin-like crystallites.¹³ Thermodynamic studies of side-chain crystallization by Jordan et al. led to the conclusion that a critical side-chain length (typically eight to nine methylene groups) is required and that the section of the side chain beyond that critical side-chain length participates in the crystallization.¹⁴ A sharp reflection at $d = \sim 4.17 \text{ \AA}$ is found in the X-ray diffraction patterns for polymers having *n*-alkyl side chains, such as poly(*n*-alkyl methacrylate)s, poly(*n*-alkylacrylate)s, poly(*n*-alkylethylene)s, poly(*n*-alkylethylene oxide)s, and so on.^{8–9,15–17}

However, our synthesized polymers (Figure 1) can form mesophases in other ways. These polymers show a rather broad wide-angle reflection at $d = 4.5\text{--}4.9 \text{ \AA}$ in the X-ray diffraction patterns, which is attributed to the spacing between side chains.¹⁷ This spacing (4.5–4.9 Å) indicates that the mesophase cannot be developed through the crystallization of the *n*-alkyl side chains. The ordered

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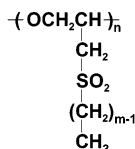


Figure 1. Molecular structure of the repeating unit of the side-chain liquid crystalline polymer, poly(oxy(*n*-alkylsulfonylethyl)methyl)ethylene). The numbers used in the abbreviations 5se, 7se, 10se, and 16se refer to the number of methylene groups in the external *n*-alkyl sequence in the side chain.

phase of these polymers was ascribed to the strong dipole–dipole interaction between the sulfone groups in the side chain.

In earlier publications on thin films with some kinds of side-chain liquid crystalline polymers, order and structure of the side-chain liquid crystalline polymer film was studied by using X-ray reflectivity and atomic force microscopy (AFM).^{18–20} However, no systematic research has been carried out on the effect of side-chain length on the orientation of side chains in thin films and the effect of side-chain conformation on adhesion properties.

In this paper, the inner structure, the surface structure, and these effects on adhesion behavior of thin films of these polymers are discussed. The vertical structure in a spin-coated thin film of the polymer was probed using X-ray reflectivity. From near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, we obtained information on the lateral structure in the top layer. The adhesion properties were evaluated using force–displacement curves by using AFM.

Experimental Section

Materials and Sample Preparation. Side-chain liquid crystalline polymers were synthesized by the method of Lee et al.²¹ As a backbone polymer, poly(oxy(chloromethyl)ethylene) (Hydrin H, Zeon Chemical Inc.) was used as the starting polymer of the synthetic procedure, and it is amorphous. Therefore, ordered properties discussed in the following part of the paper are thoroughly due to the strong dipole–dipole interaction between the sulfone groups in the side chain.²² These polymers contain an oxyethylene backbone and *n*-alkylsulfonylethyl side groups with different numbers of methylene groups ($\text{CH}_2\text{SO}_2(\text{CH}_2)_{m-1}\text{CH}_3$; $m = 5, 7, 10, \text{ and } 16$). The molecular structure of the repeating unit is depicted in Figure 1. The numbers used in the abbreviations 5se, 7se, 10se, and 16se refer to the number of methylene groups in the external *n*-alkyl sequence in the side chain (*m*). The ordered phases of these polymers were ascribed to the strong dipole–dipole interactions between the sulfone groups. These polymers have a molecular weight (M_n) of about 1.6×10^4 g/mol and M_w/M_n is 1.7, as determined by gel permeation chromatography (GPC) against a polystyrene standard.

Thin films of the polymers were prepared by spin casting on smooth silicon wafers for X-ray reflectivity, NEXAFS spectroscopy, and force–displacement curve measurements. The wafers were cleaned with “piranha” solution (70 vol % H_2SO_4 + 30 vol % H_2O_2) for 30 min at 100 °C. Before the spin casting, the wafers were dried in a nitrogen flow. The polymers were deposited on the wafer from dichloromethane by spinning at 4000 rpm for 1 min. The total thickness of the thin films was controlled by the solution concentration (0.5 wt %). The thickness of these films was about 34 nm, as determined by X-ray reflectivity. After

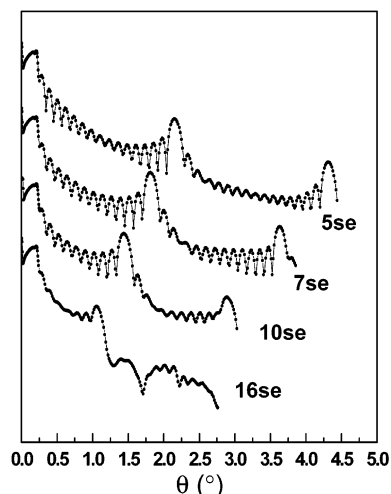


Figure 2. X-ray reflectograms for a ≈ 34 nm thick film on a silicon substrate.

preparation, the samples were annealed in the mesophasic temperature range (in between the glass transition temperature (T_g) and the isotropic transition temperature (T_i)) for 2 h.

X-ray Reflectivity. X-ray reflectivity measurements were used to analyze the inner structure in the thin film. This work was carried out at the bending magnet beam line 3C2 at the Pohang Accelerator Laboratory, Korea. X-rays of $\lambda = 1.5406$ Å monochromatized by a Si(111) double-crystal monochromator were focused at the sample position by a toroidal premirror.

NEXAFS Spectroscopy. NEXAFS spectroscopy was used to determine the side-chain conformation of the top layer in the thin films. It was carried out at the photoemission spectroscopy beam line 2B1 at the Pohang Accelerator Laboratory, Korea. The C K-edge NEXAFS spectra were obtained by total-yield mode with an electrometer (Keithley 617). The soft X-ray incident angle (θ) was varied from 20° (the electric field vector is parallel to the surface normal) to 90° (the electric field vector is parallel to the surface plane) to investigate the polarization dependence. The spectra were normalized by the adsorption-edge jump after being divided by that of the SiO_2 substrate.

Force–Displacement Curve Measurement. Force–displacement curves (f – d curves) between an AFM probe tip and thin films of side-chain liquid crystalline polymers were obtained with an atomic force microscope (AutoProbe CP Research, Park Scientific Co.). The f – d curve was obtained by recording the AFM cantilever deflection caused by the vertical movement of the AFM tip. More than 10 f – d curves were obtained at one location through repeated tip approach/retract cycles, and the measurements were also repeated at more than 10 locations for each sample. The frequency of the approach/retract cycle, 1 Hz, was chosen so as to minimize the noise fluctuation in a single f – d curve. The maximum loading force (10 nN) was kept constant for all f – d measurements, and sequential f – d curves were collected at 1 min intervals. A cantilever with a spring constant of 0.4 N/m and a silicon conical tip (radius of curvature, ≈ 10 nm) was used for all measurements. Individual force calibrations were performed. Other parameters of the f – d measurement such as the tip extending–retracting range and the optical path alignment were also kept unchanged during the experiments.

Results and Discussion

A. The Structure of a Poly(oxy(*n*-alkylsulfonylethyl)methyl)ethylene) Thin Film. The inner structure of thin films of the side-chain liquid crystalline polymers with different side-chain lengths was analyzed by X-ray reflectivity. The reflectivity data of the thin films presented in Figure 2 were obtained at room temperature after annealing in the mesophase for 2 h. The reflectivity patterns of the thin films show both Kiessig fringes and Bragg peaks. Kiessig fringes are caused by interference of beams reflected at the air–polymer and polymer–

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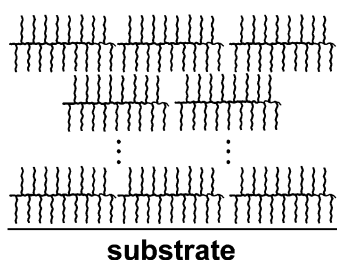
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Scheme 1. Two-Dimensional Scheme Illustrating Alternating Layers of an Oxyethylene Backbone with an *n*-Alkylsulfonylethylmethyl Side Group (5se, 7se, and 10se)



substrate interfaces, respectively.²³ The total thickness of the film can be derived from the distance between subsequent maxima of the fringes (≈ 34 nm). The Kiessig fringes due to the film thickness are modulated by the Bragg peak. This peak is caused by a periodic density modulation perpendicular to the surface and is taken as representative of the formation of the ordered smectic phase.^{24,25} From this Bragg peak, arising from the periodicity of layers, the layer thickness in the film was obtained. The layer thickness determined by X-ray reflectivity is approximately double the size of the calculated length of the side chain when the side chains are fully extended. This calculation was done by summation over the atom-atom distances in the side chain. These results indicate that the inner structure of the thin film forms a bilayer structure as depicted in Scheme 1.²⁶ In this calculation, only the side-chain length was considered. If we consider the occupied volume of the backbone, the slight tilting of side chains could be expected. Similar structures were recently found in thin films of side-chain crystalline polymers, side-chain liquid crystalline polymers such as perfluoroalkyl methacrylate,²⁷ alternating copolymers of maleic anhydride and α -olefins carrying terminal mesogenic methoxybiphenyloxy groups,²⁸ and other polymers.²⁹⁻³¹

In the case of 5se, 7se, and 10se, the second Bragg peaks as well as the first Bragg peak are observed. Also, high-frequency oscillations of Kiessig fringes are observed. However, in the case of 16se thin film the intensity of the Bragg peak dramatically decreases and there is no second Bragg peak. The modulation of Kiessig fringes is not clear as well. These results lead us to conclude that the change in the structure of the thin film occurs as the side chain is longer than the critical value. The critical length of the side chain is between $m = 11$ and $m = 16$. Since the position of the sulfone group in the side chain is identical, the difference of the order and structure in thin films is due to the difference in the number of methylene groups in the side chain. The layered structure in 16se thin film is less perfect. Also, the air-polymer surface and the interface between layers are not smooth. From these

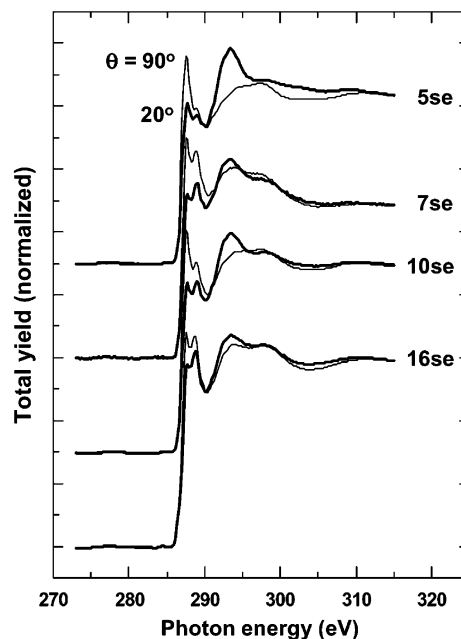


Figure 3. Series of high-resolution NEXAFS spectra of the C 1s edge of thin films of side-chain liquid crystalline polymers. The spectra were recorded for different angles of incidence, θ , of incoming photons.

results, it can be expected that side chains are presumably loosely oriented when the alkyl chain length in the side group is longer than the critical length.

NEXAFS spectroscopy was used to determine the side-chain conformation near the top surface of the thin film. It is a powerful tool for the determination of molecular orientation at a surface.³² Figure 3 shows a series of NEXAFS spectra for two different incident angles at room temperature. The spectra are dominated by two resonances which originate from the C-H/Rydberg and C-C σ^* orbitals. The sharp features situated at 287.7 and 288.8 eV originate from transitions into several Rydberg states, with dipole transition moments lying in the plane of the C-H balance orbitals.³³ This assignment has been confirmed by semiempirical $X\alpha$ calculations on propane. These calculations also indicated that the C-H resonance is split into a C-H_o and a C-H_r component, with a 1.1 eV higher excitation energy for the latter. Their intensities for normal X-ray incidence ($\theta = 90^\circ$) are stronger than those for grazing incidence ($\theta = 20^\circ$). The broader resonance around 293.3 eV can be assigned to transitions into the C-C σ^* orbital.³⁴ Its intensity for grazing X-ray incidence is stronger than that for normal incidence. The transition into C-H/Rydberg and C-C σ^* orbitals shows an opposite polarization dependence with incident angles. However, the opposite polarization dependence of 16se thin film is relatively weaker than that of 5se, 7se, and 10se. From these results, we can expect that the side chains in the surface layer of 5se, 7se, and 10se are oriented almost perpendicularly to the surface (Scheme 1). However, a slight tilting of the side chains would be expected to obtain the spacing between side chains (4.5–4.9 Å). On the other hand, side chains in the surface layer of 16se are presumably loosely oriented, corresponding to the side-chain conformation of the inner structure.

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Also, the thermal analysis with differential scanning calorimetry (DSC) confirms the proposed scheme. The isotropic transition temperatures of 5se, 7se, and 10se are 120.9, 125.3, and 143.7 °C, respectively. As the number of methylene units in the side chain increases, the isotropic transition temperature increases. However, the isotropic transition temperature decreases when the alkyl chain length in the side group is longer than the critical length (16se, 115.2 °C). The decrease of the isotropic transition temperature with increase of the side-chain length beyond a critical length would be ascribed to the loose orientation of side chains.

When the number of methylene groups in the external *n*-alkyl sequence in the side chain is greater than the critical value, the influence of the interaction between SO₂ groups decreases. The alkyl groups at the end of the side chain cannot be packed densely. Therefore, side chains are relatively mobile. The change in the side-chain conformation of the thin film causes an increase in the nanoscale viscoelastic dissipation during the detachment of the AFM tip from the film, which in turn causes a dramatic change in the adhesion behavior of the polymer film. This will be discussed in the following session.

B. Effect of Side-Chain Conformation on Adhesion Force. AFM was used to investigate the effect of side-chain conformation on the adhesion behavior of the thin films. AFM is a useful tool in investigating mechanical interactions occurring at sample/tip interfaces at nanodimensions.³⁵ Penetration depths are only several nanometers. In the case of molecular level contact using an AFM probe tip, the change of near-surface properties in thin films drastically affects adhesion behavior. The force–displacement curves of side-chain liquid crystalline polymer thin films are presented in Figure 4a. The *f*–*d* curve for the samples was obtained from the following processes.³⁶ First, the cantilever approaches the sample surface. Typically, the cantilever shows no deflection and zero force is recorded. Second, the tip makes contact with the surface and pushes against the surface. The cantilever is bent up with the applied force. Finally, the tip is withdrawn from the surface. The cantilever is bent down until the tip reaches a distance at which the contact between tip and sample becomes broken. Then, the cantilever deflection reverts to the original condition in the noncontact region. The difference between this minimal force and the zero force is defined as adhesion force.

Figure 4b represents adhesion forces of side-chain liquid crystalline polymer thin films. The 5se, 7se, and 10se films have similar adhesion forces (3.9–5.0 nN). However, the adhesion force of 16se film is relatively higher (13.2 nN). According to the well-known empirical formalism of Gent and Schultz, adhesion energy is attributed to an additive combination of the intrinsic work of adhesion associated with the surface properties and the viscoelastic dissipation energy of the adhesives incurred by the deformation of the material.³⁷ In the case of 5se, 7se, and 10se films, the CH₃ groups are exposed at the surface because of the perfect orientation of the side chains. The surface of the 16se film is presumably composed of CH₂ and CH₃ groups. The surface energy of all samples is very similar (27 mJ/m²). Therefore, the abrupt change of adhesion force is caused by the viscoelastic energy dissipation when the same contact force (10 nN) is loaded.

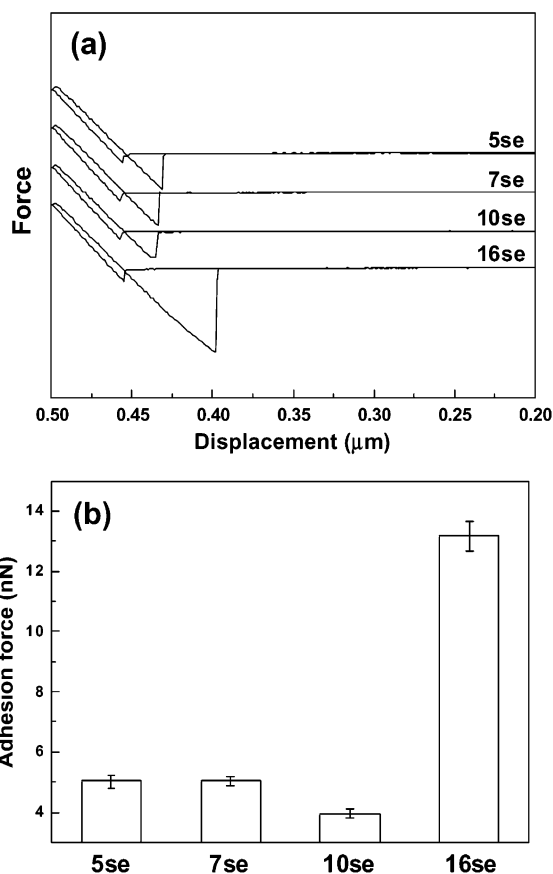


Figure 4. (a) Representative force vs displacement curves between the silicon tip and side-chain liquid crystalline polymer thin films (5se, 7se, 10se, and 16se) by using AFM. (b) Statistical results of adhesion force measured by AFM.

In the case of 5se, 7se, and 10se films, the penetration depth of the silicon tip may be small because of the low chain mobility resulting from the perfect orientation of the side chains. There is small viscoelastic deformation of the sample during the detachment of the tip from the film, which results in low adhesion force. On the other hand, in the case of 16se thin film, side chains in the surface layer are relatively mobile and are deformed more easily. The penetration depth of the tip may be relatively deep. This leads to an increase in the intimate molecular contact at the tip/film interface, which in turn increases the contact area between the tip and the film. These induce a relatively large amount of viscoelastic dissipation during the detachment of the tip from the film. Therefore, the adhesion force increases considerably. The results of the force–displacement curve confirm that side chains are loosely oriented when the alkyl chain length in the side group is longer than the critical length. It can be expected that the critical length of the side chain is between $m = 11$ and $m = 16$.

Summary and Conclusions

The inner structure and surface properties of a side-chain liquid crystalline polymer thin film spin-coated onto a silicon wafer were characterized, and the adhesion behavior of this film was shown to be correlated with its structure.

X-ray reflectivity studies of the material below the glass transition temperature indicated that the inner part of the thin film has a bilayer structure. However, side chains in the thin film are loosely oriented when the number of methylene groups in the external *n*-alkyl sequence in the

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side chain (m) is larger than the critical length of the side chain (between $m=11$ and $m=16$). NEXAFS spectroscopy results showed that the side chains near the surface are loosely oriented when m is larger than the critical value. The interaction between SO_2 groups cannot dominate the orientation of the side-chain end when the number of methylene groups in the external n -alkyl sequence in the side chain is more than the critical value. Therefore, the alkyl groups at the end of the side chain cannot be packed densely, but are loosely oriented.

Force-displacement curves measured by AFM show that the loose orientation of side chains leads to an increase in the ability of the film to dissipate energy during the detachment of the tip from the film, resulting from an

increase in the degree of molecular contact between the film and the tip. These effects contribute to the dramatic increase in adhesion force.

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