Macromolecules **2003,** *36,* 2009−2014

Switchable Tack in Side-Chain Liquid Crystalline Polymers[†]

Kilwon Cho,* Jeong Ho Cho, Soong Yoon, and Chan Eon Park

Department of Chemical Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea

Jong-Chan Lee and Se-Hui Han

School of Chemical Engineering, Seoul National University, Seoul 151-744, Korea

Ki-Bong Lee and Japil Koo

Department of Physics, Pohang University of Science and Technology, Pohang 790-784, Korea

Received September 11, 2002; Revised Manuscript Received January 9, 2003

ABSTRACT: With the aim of developing a material with switchable tack properties, a side-chain liquid crystalline polymer containing a poly(oxyethylene) backbone and *n*-heptylsulfonylmethyl side chains was synthesized. The inner structure, surface properties, and tack behavior of this polymer film were investigated. An X-ray reflectivity study of a film of the polymer 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. The layer thickness is roughly twice the length of the fully extended side chain, indicating a double-layered structure of the polymer with side chains normal to the polymer backbone having an almost all-trans conformation. The contact angle decreases abruptly at the isotropic transition temperature, which results from the disappearance of the smectic order. The coiling of the polymer backbone and disordering of side chains occur above the isotropic transition temperature. NEXAFS spectroscopy and AFM results confirmed that at temperatures below the isotropic transition temperature the side chains in the top layer are oriented such that they are almost perpendicular to the surface, which results in the packing of the CH_3 groups at the surface and hence a very low surface energy. A remarkable change in tack properties is observed at the smectic-to-isotropic transition temperature. The dramatic change in tack properties, which occurs within a narrow temperature range, is due to the change in the surface energy and viscoelastic behavior of the film. This reversible and dramatic change in the tack force over a narrow temperature range could potentially be exploited in applications that require materials with switchable tackiness.

Introduction

Tack is the ability of a material to adhere instantaneously to a solid surface when the two materials are brought into contact under light pressure for a short time.[1] According to the well-known empirical formalism of Gent and Schulz, tack 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.[2,3] Therefore, to change the tack behavior, it is necessary to modify the surface properties and viscoelastic properties of the adhesives.

At the glass transition temperature, the viscoelastic dissipation energy changes but the surface properties remain unchanged. Therefore, the tack properties of conventional adhesives used for household and most industrial purposes change broadly at the glass transition temperature.[4] These materials cannot satisfy the need of an engineering interface that requires special properties at specific processing conditions. For example, adhesives used in a semiconductor dicing and grinding process or in some biomedical processes require a switchable tack property. The tack property, which changes sensitively with a small change of environmental conditions, i.e., temperature, pressure, and pH, is called a switchable tack. To gain such a property, tailoring the molecular parameters that influence tack is required not only by modifying the surface properties but also by controlling its viscoelastic properties.[5]

Side-chain liquid crystalline polymers are one of the candidates for satisfying these properties.[6] The structure of these polymers dramatically changes from a highly ordered state to a disordered state at the isotropic transition temperature. Recently, Crevoisier et al. reported the wetting and tack properties of a side-chain liquid crystalline copolymer containing poly(acrylate) with a long perfluoroalkyl side chain and poly(methacrylate) with a long alkyl chain.[7] They found that below the isotropic transition temperature of the copolymer the perfluoroalkyl side chains are segregated to the surface, and above the transition temperature a surface rearrangement occurs in which alkyl segments move to the surface. In addition, the material undergoes a bulk transition between a highly ordered state and a disordered state that is accompanied by a change from rigid to soft behavior. The change of the surface and bulk mechanical properties dramatically alters tack behavior. However, no systematic research has been carried out to elucidate the temperature-dependent surface and inner structures of films of side-chain liquid crystalline polymers, nor has the correlation between these structures and the tack behavior been studied.

In the present study, we synthesized a side-chain liquid crystalline polymer in which the side chain and main chain have different surface characteristics. The backbone is hydrophilic poly(oxyethylene), and the side

---

[†] Dedicated to Professor Won-Jei Cho for his 65th birthday.

* To whom all correspondence should be addressed. E-mail: kwcho@postech.ac.kr.

10.1021/ma025666n CCC: $25.00

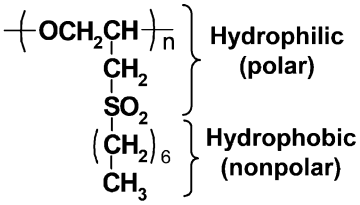

Figure 1. Molecular structure of the repeating unit of the side-chain liquid crystalline polymer, poly(oxy(*n*-heptylsulfonylmethyl)ethylene) (LCP-7se).

chain is hydrophobic *n*-heptylsulfonylmethyl. Generally, side-chain liquid crystalline polymers have a flexible backbone with mesogenic side groups.[8−10] The polymer considered in the present study lacks stiff, rodlike mesogens but still exhibits an ordered phase. The ability of this polymer to form an ordered phase is attributed to the strong dipole−dipole interaction between the sulfone groups.[11] This polymer undergoes a bulk transition between a highly ordered smectic phase and an isotropic phase at the isotropic transition temperature. This dramatic structural change over a narrow temperature range is accompanied by a change in the viscoelastic properties.[12,13] In addition, the surface properties of this polymer change dramatically at the transition temperature because the transition process modifies the composition of side-chain groups and main-chain groups at the surface, and these groups have different surface characteristics. Therefore, the dramatic changes in the surface properties and bulk viscoelastic properties of this polymer result in switchable tack behavior over a narrow temperature range.

In this paper, the inner structure, surface properties, and tack behavior of this polymer film are discussed. The vertical structure in a film of the polymer coated onto a silicon wafer was probed using X-ray reflectivity. From atomic force microscopy (AFM) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, we obtained information on the lateral structure in the top layer. The temperature dependence of the surface properties was analyzed using X-ray reflectivity and contact angle measurements. The tack properties were evaluated using the probe tack test.

Experimental Section

Materials and Sample Preparation. The side-chain liquid crystalline polymer studied here was synthesized by Lee et al.[14] This polymer contains an oxyethylene backbone and *n*-heptylsulfonylmethyl side groups (Figure 1). It has side-chain liquid crystalline characteristics because of the strong dipole−dipole interactions between the polar sulfone groups in the side chains. Its molecular weight (M_n) is 1.59×10^4 g/mol and M_w/M_n is 1.71, as determined by GPC against polystylene standard. The formation of a mesophase was established by differential scanning calorimetry (DSC), polarizing optical microscopy, and X-ray diffraction measurements. Below 54 °C, the polymer is glassy. Between 54 and 125 °C, it organizes in a smectic A phase, and above 125 °C it is isotropic.

Thin films of the polymer were prepared by spin-casting onto a smooth silicon wafer. The polymers were deposited onto the silicon wafer from dichloromethane by spinning at 6000 rpm for 1 min. After preparation, the samples were annealed at 90 °C (mesophase) for 1 h. The thickness of these films was about 293 Å, as determined by X-ray reflectivity. These films were used for the X-ray reflectivity, NEXAFS spectroscopy, AFM, and contact angle measurements. The samples for the probe tack test were prepared by solvent-casting and annealed at 90 °C for 1 h. The film thickness was about 50 μm.

X-ray Reflectivity. X-ray reflectivity was used to analyze the structure inside the thin film. The measurements were carried out using the bending magnet beam line 3C2 at the Pohang Light Source, Korea. X-rays of wavelength $\lambda = 1.5406$ Å monochromatized by a Si(111) double-crystal monochromator were focused at the sample position by a toroidal premirror. Temperature-dependent X-ray reflectivity measurements were performed in a heating chamber under a nitrogen atmosphere. During the experiments, the temperature was measured directly on the sample.[15]

NEXAFS Spectroscopy. NEXAFS spectroscopy was used to determine the surface orientation of the *n*-heptylsulfonylmethyl side chains. These measurements were carried out using the photoemission spectroscopy beamline 2B1 at the Pohang Light Source, Korea. The C K-edge NEXAFS spectra were obtained in the total-yield mode with an electrometer (Keithley 617). To investigate the polarization dependence, the incident angle (θ) of the soft X-rays was varied from 20° (electric field vector parallel to the surface normal) to 90° (electric field vector parallel to the surface plane). In addition, the spectra were normalized by the adsorption-edge jump after being divided by that of the SiO_2 substrate.

AFM. The surface topography of the thin film was investigated by AFM at room temperature. AFM images were measured using an Autoprobe CP scanning probe microscope (Park Scientific Instruments) operated in contact mode at a set force of 2.5 nN. A silicon cantilever with a spring constant of 0.24 N/m was used, and the scan rate was 0.5 Hz.

Contact Angle Measurement. The temperature dependence of the contact angle against glycerol was investigated using the sessile drop technique (Krüss BSA10). Measurements were performed in a heating chamber; the temperature of the air in this chamber was approximately equal to that of the substrate. The angles reported are the average values of five measurements, where a different droplet was used for each measurement.

Rheological Properties. The temperature dependence of the storage modulus (G') was investigated by a Rheometrics dynamic spectrometer (RDSll, Rheometrics) with parallel plates of 8 mm diameter. A dynamic temperature sweep experiment was done under isochronal conditions with increasing temperature from 100 to 135 °C. The heating rate was 0.5 °C/min. The strain amplitude and the angular frequency were 0.05 and 0.05 rad/s, respectively. This condition lies in a linear viscoelastic region.

Probe Tack Test. The probe tack test was used to measure the tack force of the polymer. The test was conducted on the probe tack tester (Texture Analyzer TX-2i) with a polished stainless steel probe 3 mm in diameter, which was designed to measure the tack force as a function of time. Measurements were performed at six different temperatures under a constant force of 5 N, a probe speed of 0.5 mm/s, and a dwell time of 1 s. The tack force was obtained from the maximum point in the curve of F vs t. The test results reported here are the average of four measurements under the same conditions.

Results and Discussion

Structure of a Poly(oxy(*n*-heptylsulfonylmethyl)ethylene) Thin Film. The structure inside the thin film with smectic layers was analyzed using X-ray reflectivity. The reflectivity data of the thin film presented in Figure 2 were obtained at room temperature after annealing at 90 °C (mesophase) for 1 h. Both Kiessig fringes and Bragg peaks were observed in the reflectivity pattern of the thin film. Kiessig fringes are caused by interferences of beams reflected at the air−polymer and polymer−substrate interface.[16] The total thickness of the film can be derived from the distance between subsequent maxima of the fringes (≈293 Å). The Kiessig fringes due to the film thickness are modulated by Bragg peaks at $\theta = 1.83°$ and 3.69°. These peaks are caused by a periodic density modulation perpendicular to the surface and are taken as representative of the formation of the ordered smectic

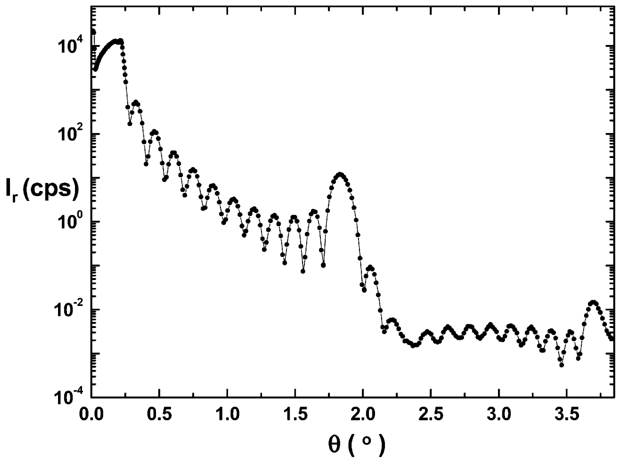

Figure 2. Reflected X-ray intensity, I_r, as a function of the angle of incidence, θ, for an ≈29 nm thick film annealed at 90 °C for 1 h on a silicon substrate.

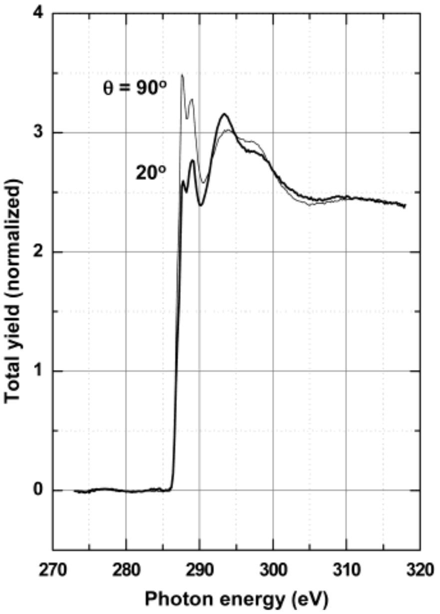

Figure 3. Series of high-resolution NEXAFS spectra of the C 1s edge of the LCP-7se on a silicon substrate recorded for different angles of incidence, θ, of incoming photons.

phase.[17,18] From these Bragg peaks, which arise from the periodicity of layers, the layer thickness was determined to be about 24 Å. This value is approximately double the extended length of the side chain, as calculated by summing over the atom−atom distances in the side chain. These results indicate that the polymers inside the thin film form a bilayer structure as depicted in Figure 5. Similar structures were recently found in thin films of side-chain crystalline polymers, side-chain liquid crystalline polymers such as perfluoroalkyl methacrylate,[19] alternating copolymers of maleic anhydride and α-olefins carrying terminal mesogenic methoxybiphenyloxy groups,[20] and other polymers.[21,22]

It is difficult to characterize the structure of the region close to the substrate using X-ray reflectivity. We expect that the side chains close to the substrate will be oriented with their axes normal to the substrate because the total thickness of the film is an integer multiple of the layer thickness (i.e., the film thickness of 293 Å is approximately 12 times the layer thickness). It is probable that the good adhesion properties of the backbone with the polar silicon substrate will cause the side chains to be loosely packed close to the substrate. However, the side-chain configuration in the first layer adjacent to the substrate remains a matter of speculation.[23]

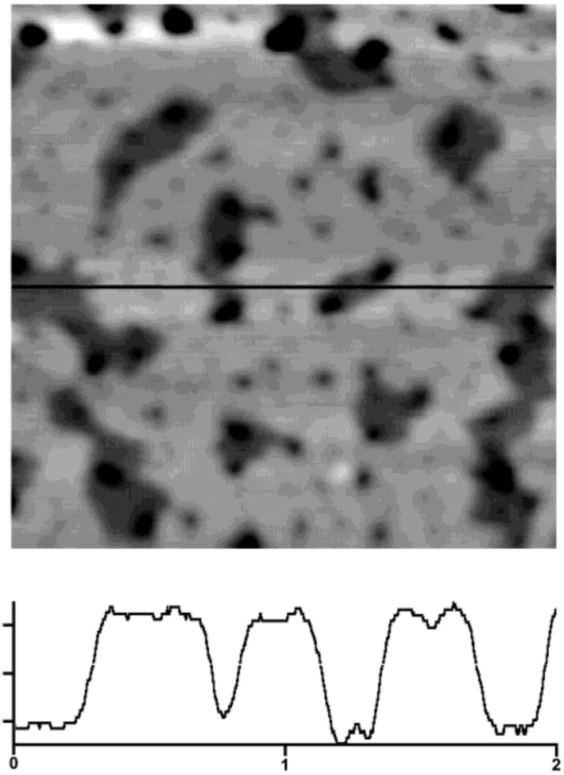

Figure 4. AFM image (2 × 2 μm^2) of an ≈29 nm thick film on silicon substrate and the cross-sectional profile along the line in the image.

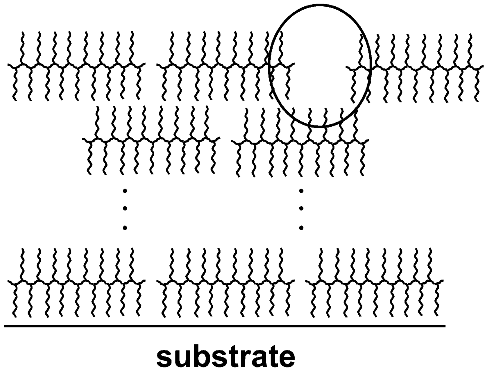

Figure 5. Two-dimensional scheme illustrating alternating layers of an oxyethylene backbone and *n*-heptylsulfonylmethyl side group. The solid circle indicates holes of AFM image.

NEXAFS spectroscopy and AFM were used to determine the chain conformation in the top layer of the thin film. NEXAFS spectroscopy is a powerful tool for the determination of molecular orientation at a surface.[24] Figure 3 shows a series of NEXAFS spectra for two different incident angles, 90° and 20°, at room temperature. The spectra are dominated by two resonances, originating 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.[25,26] This assignment has been confirmed by semiempirical Xα calculations on propane. These calculations also indicated that the C−H resonance is split into C−H$_\sigma$ and C−H$_\pi$ components, where the excitation energy of the latter component is 1.1 eV higher. The intensities of these components at normal X-ray incidence ($\theta = 90°$) are stronger than those at grazing incidence ($\theta = 20°$). The broader resonance at around 293.3 eV can be assigned to transitions into the C−C σ^* orbital.[27] Its intensity at grazing X-ray incidence is stronger than that at normal incidence. The transitions into the C−H/Rydberg and C−C σ^* orbitals show an opposite polarization dependence with changing incident angle. These results demonstrate that the side chains in the surface layer are oriented almost perpendicular to the surface, with the CH_3 groups exposed at the surface. Similar results have been reported for thin films of perfluoroalkyl methacrylate[19] and other polymers.[28]

Figure 4 shows the surface topography of the thin film and the cross-sectional profile along the line indicated in the image. The surface of the film is covered in holes and terrace-like structures with a characteristic height of 24 ± 1 Å. Several factors could potentially cause the structure observed on the top surface. One possibility is that the holes formed due to lateral shrinkage of the surface layer resulting from improved packing of the side chains after evaporation of the solvent.[19] A more plausible explanation is that the holes formed because there was insufficient material for a complete top layer.[16] It should be noted that this structure is ascribed to bilayer formation in which the side chains in the top layer are in a rather extended conformation and oriented perpendicular to the surface. In addition, the characteristic height measured using AFM (24 ± 1 Å) is approximately equal to the layer thickness calculated from the X-ray reflectivity data, which was found to correspond to the bilayer spacing. The fact that the characteristic height of the structure corresponds to one bilayer spacing indicates that the side chains are alternately directed up and down. The CH_3 groups are exposed at the surface due to the almost perfect orientation of the side chains perpendicular to the surface. The high value of the contact angle of the film surface against glycerol at room temperature, which is discussed in a later section, is consistent with the proposed surface structure. Figure 5 shows a schematic representation of the film structure as deduced from the experimental data discussed so far.

Temperature-Dependent Surface Properties. The variation in film structure with changing temperature was analyzed using X-ray reflectivity and contact angle measurements. Figure 6 shows the X-ray reflectivity curves at a range of temperatures. The Bragg peak is observed at temperatures below the isotropic transition temperature of the polymer (125 °C), but only Kiessig fringes are visible above the transition temperature. From this behavior, we deduce that smectic order exists below the isotropic transition temperature, but this order vanishes above the transition temperature. The layer structure re-forms on cooling the system from the isotropic regime,[29] confirming that the transition is reversible.

Figure 7a shows the temperature dependence of the contact angle of the thin film against glycerol obtained using the sessile drop technique. Glycerol is a polar hydrophilic solvent. The contact angle remains constant upon raising the temperature up to the isotropic transition temperature of 125 °C. As discussed above, reflectivity data indicate the presence of smectic order in the film below the transition temperature, and the presence of smectic order indicates the regular arrangement of the CH_3 groups at the top surface. Thus, a large contact angle against glycerol is observed below the transition temperature because the glycerol is in contact with the nonpolar and hydrophobic CH_3 groups. When the temperature is raised to above the transition temperature, however, the contact angle abruptly decreases (Figure 7a) due to the loss of smectic order. Increase of the temperature to above the transition temperature results in coiling of the polymer backbone and disordering of the side chains. This causes the CH_2, SO_2, and poly(oxyethylene) groups to be exposed at the surface, resulting in a significant increase in the polar and hydrophilic properties of the surface.[30] The change in the surface properties of the film at the isotropic transition temperature causes a dramatic increase in the surface energy, which in turn causes a dramatic change in the tack behavior of the polymer film.

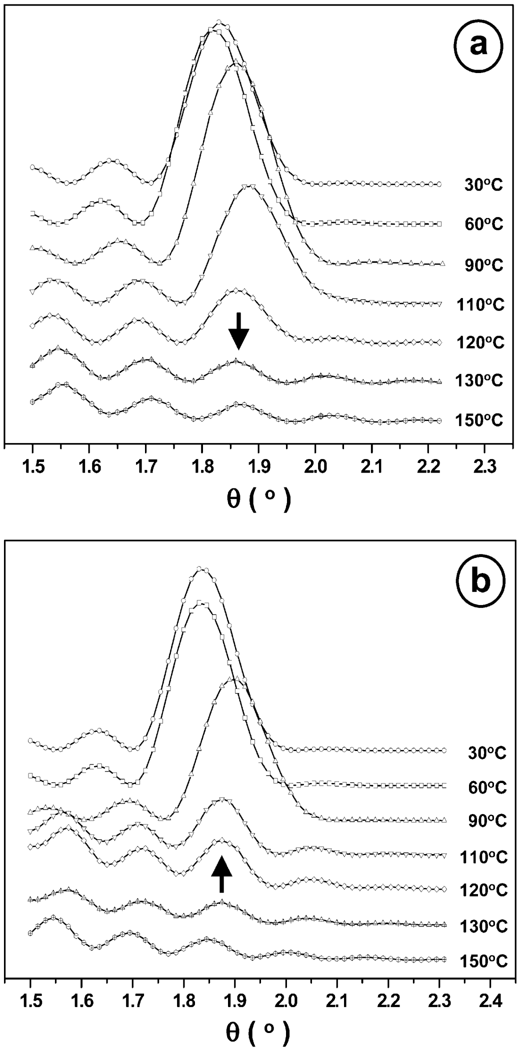

Figure 6. Temperature-dependent X-ray reflectograms: (a) heating, (b) cooling.

Tack Behavior. A thick film of thickness of 50 μm was used for the probe tack test. It was prepared by solvent-casting and annealed at 90 °C for 1 h. The inner structure of thick film was investigated by using X-ray reflectivity. The Bragg peak ($\theta = 1.78°$) was observed in the reflectivity pattern of the 50 μm thick film. From the Bragg peak, the layer thickness was determined to be about 25 Å. This value is almost the same as the layer thickness for the thin film. These results indicate

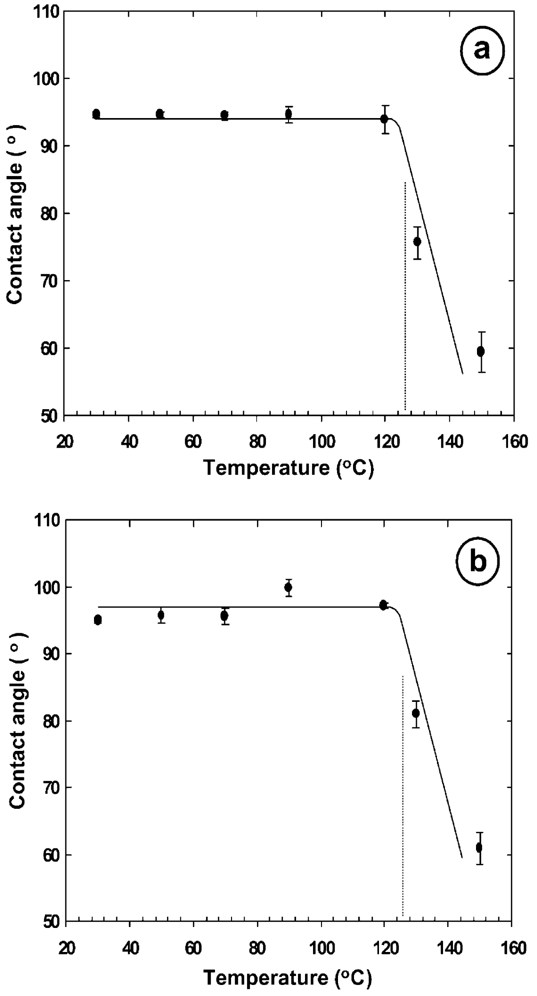

Figure 7. Sessile drop contact angle of the LCP-7se film against glycerol as a function of temperature: (a) thin film (≈29 nm), (b) thick film (≈50 μm). The dotted line indicates the isotropic transition temperature (125 °C) of the polymer.

that the polymers inside the thick film also form a bilayer structure like the thin film. Figure 7b shows the temperature dependence of contact angle of the thick film against glycerol. The result is very similar to that of the thin film. The contact angle (95°) on the surface of the thick film at room temperature is the same as that of the thin film, which indicates that the CH_3 groups are exposed at the surface. The contact angle abruptly decreases as the temperature is raised to above the isotropic transition temperature. The change in the surface properties at the transition temperature causes a dramatic increase in the surface energy like the thin film. The order and surface properties of the side-chain liquid crystalline polymer film are not much affected by the total film thickness within our experimental range.

Figure 8 shows the temperature dependence of the tack force measured using the probe tack test. The tack force drastically increases at the isotropic transition temperature (125 °C). Several factors could potentially cause the dramatic change in the tack force at the transition temperature, including the surface energy, surface roughness, and intimate molecular contact as well as the dissipative ability of the film.

One factor expected to affect the tack behavior is the increase in the surface energy caused by the phase transition. Below the transition temperature, the polymers at the surface are ordered into a smectic phase with CH_3 groups at the surface. This structure has a low surface energy and hence a low tack force. Above the transition temperature, CH_2, SO_2, and poly(oxyethylene) groups are exposed at the surface. This causes the surface energy to increase, which induces strong interfacial interactions between the probe and the film. A second factor that will affect tack behavior is the surface roughness and intimate molecular contact at the interface. The disordering of the backbone and the side chains at the transition temperature causes the film to soften and reduces the surface roughness. The softening of the films leads to increase the intimate molecular contact at the probe/film interface, which in turn increases the contact area between the probe and the film. This results in an increase in the tack force.[7,31] Finally, the viscoelastic dissipation characteristics of the surface should be considered. Rheological properties in Figure 9 show that G' drops precipitously at the transition temperature. Therefore, the energy is dissipated due to the viscoelastic deformation of the soft body when a probe is pulled away from a soft and highly viscoelastic

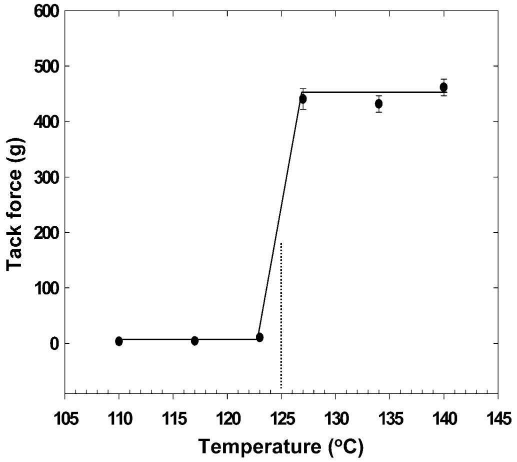

Figure 8. Probe tack results showing the tack force as a function of temperature for a contact time of 1 s. The dotted line indicates the isotropic transition temperature of the polymer (125 °C).

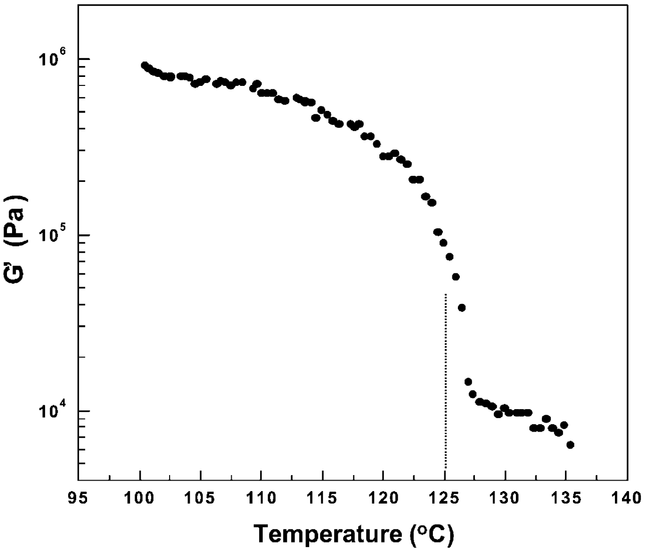

Figure 9. Temperature sweep of G' at a heating rate of 0.5 °C/min for the LCP-7se. The frequency and strain amplitude are 0.05 rad/s and 0.05, respectively. The dotted line indicates the isotropic transition temperature (125 °C) of the polymer.

material.[31,32] Above the transition temperature, the film becomes soft, and hence the dissipative ability of the film increases. The strong interaction between the probe and the film caused by the change of the surface composition and softening of the film induces a large amount of viscoelastic dissipation during the detachment of the probe from the film. Therefore, the tack force increases abruptly at the transition temperature.

Summary and Conclusions

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

X-ray reflectivity studies of the material below the isotropic transition temperature indicated that in this temperature regime the inner part of the film has a bilayer structure and that the spacing of these bilayers is the same as that of a bulk sample of the polymer (≈24 Å). NEXAFS spectroscopy and AFM results showed that the side chains in the top layer of this bilayer structure are oriented such that they are almost perpendicular to the surface. Regular arrangement of the side chains indicates the packing the CH_3 groups at the surface. The exposure of CH_3 groups at the surface results in a low surface energy.

Temperature-dependent X-ray reflectivity and contact angle measurements showed that heating the material to temperatures above the isotropic transition temperature (125 °C) causes CH_2, SO_2, and poly(oxyethylene) groups to become exposed at the surface. The abrupt change in the surface composition at the transition temperature is accompanied by an abrupt increase in the surface energy, which causes a dramatic increase in the tack force. Additionally, the change in viscoelastic properties that occurs at the transition from the ordered smectic structure to an isotropic structure leads to an increase in the ability of the film to dissipate energy and also to an increase in the degree of molecular contact between the film and the probe. These effects contribute to the dramatic increase in tack force at the transition temperature. This reversible and dramatic change in the tack force over a narrow temperature range could potentially be exploited in applications that require materials with switchable tackiness. This switchable tack property could be enhanced by developing polymers with larger differences in surface energy between the backbone and the side chain.

Acknowledgment. The authors thank the Ministry of Science and Technology of Korea (National Research Laboratory Project) and the Ministry of Education of Korea (BK21 Program) for their financial support and the Pohang Accelerator Laboratory for providing the 2B1, 3C2, and 4C2 beamlines used in this study.

References and Notes

(1) Satas, D. *Handbook of Pressure Sensitive Adhesive Technology and Application*; Satas & Associates: Warwick, 2002; p 36.
(2) Gent, A. N.; Shultz, J. *J. Adhes.* **1972**, *3*, 281.
(3) Andrews, E. H.; Kinloch, A. J. *Proc. R. Soc. London, Ser. A* **1973**, *332*, 385.
(4) Zosel, A. *Colloid Polym. Sci.* **1985**, *263*, 541.
(5) Russell, T. P.; Kim, H. C. *Science* **1999**, *285*, 1219.
(6) Koberstein, J. T.; et al. *J. Adhes.* **1998**, *66*, 229.
(7) de Crevoisier, G.; Fabre, P.; Corpart, J. M.; Leibler, L. *Science* **1999**, *285*, 1246.
(8) McArdle, C. B. *Side Chain Liquid Crystal Polymers*; Chapman and Hall: New York, 1989.
(9) Noirez, L.; Boeffel, C.; Daoud-Aladine, A. *Phys. Rev. Lett.* **1998**, *80*, 1453.
(10) Mallon, J. J.; Kantor, S. W. *Macromolecules* **1989**, *22*, 2077.
(11) Lee, J. C.; et al. *Macromol. Rapid Commun.* **2001**, *22*, 815.
(12) Rottink, B. H.; te Nijenhuis, K.; Addink, R.; Mijs, W. J. *Polym. Bull. (Berlin)* **1993**, *31*, 221.
(13) Yamaguchi, T.; Asada, T.; Koide, N. *Mol. Cryst. Liq. Cryst.* **1992**, *214*, 1.
(14) Lee, J. C.; Litt, M. H.; Rogers, C. E. *Macromolecules* **1998**, *31*, 2440.
(15) Mensinger, H.; Stamm, M.; Boeffel, C. *J. Chem. Phys.* **1992**, *96*, 4.
(16) van der Wielen, M. W. J.; Cohen Stuart, M. A.; Fleer, G. J. *Langmuir* **1997**, *13*, 4762.
(17) Vix, A. B. E.; Müller-Buschbaum, P.; Stocker, W.; Stamm, M.; Rabe, J. P. *Langmuir* **2000**, *16*, 10456.
(18) Hamley, I. W.; Imlie, C. T. *J. Mater. Sci., Lett.* **1998**, *17*, 339.
(19) Sheiko, S.; Lermann, E.; Möller, M. *Langmuir* **1996**, *12*, 4015.
(20) van der Wielen, M. W. J.; Cohen Stuart, M. A.; Fleer, G. J.; Schlatmann, A. R.; de Boer, D. K. G. *Phys. Rev. E* **1999**, *60*, 4252.
(21) Schwickert, H.; Strobl, G.; Kimmig, M. *J. Chem. Phys.* **1991**, *95*, 2800.
(22) Russell, T. P.; Rabolt, J. F.; Twieg, R. J.; Siemens, R. L.; Farmer, B. L. *Macromolecules* **1986**, *19*, 1135.
(23) Cull, B.; Shi, Y.; Kumar, S.; Shih, R.; Mann, J. *Phys. Rev. Lett.* **1995**, *51*, 526.
(24) Stöhr J. *NEXAFS Spectroscopy*; Springer-Verlag: Heidelberg, 1992.
(25) Bagus, P. S.; Weiss, K.; Schertel, A.; Wöll, Ch.; Braun, W.; Hellwig, C.; Jung, C. *Chem. Phys. Lett.* **1996**, *248*, 129.
(26) Weiss, K.; Bagus, P. S.; Wöll, Ch. *J. Chem. Phys.* **1999**, *111*, 6834.
(27) Outka, D. A.; Stöhr, J.; Rabe, J. P.; Swalen, J. D. *J. Chem. Phys.* **1988**, *88*, 4076.
(28) Hähner, G.; Kenzler, M.; Wöll, Ch.; Grunze, M.; Scheller, M. K.; Cederbaum, L. S. *Phys. Rev. Lett.* **1991**, *67*, 851.
(29) Elben, H.; Strobl, G. *Macromolecules* **1993**, *26*, 1013.
(30) Wang, J.; Mao, G.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1997**, *30*, 1906.
(31) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.
(32) Lakrout, H.; Sergot, P.; Creton, C. *J. Adhes.* **1999**, *69*, 307.

MA025666N