LC Alignment Behaviors at Rubbed Films of Brush Polyimides: Perpendicular LC Alignment versus Parallel LC Alignment

Taek Joon Lee, Seok Gyu Hahm, Seung Woo Lee, Boknam Chae, Seong June Lee, Seung Bin Kim, Jin Chul Jung, and Moonhor Ree
Department of Chemistry, Division of Molecular and Life Sciences, BK21 Program, Center for Integrated Molecular Systems, Polymer Research Institute, Department of Materials Science and Engineering, Pohang University of Science & Technology, San 31, Hyoja-dong, Nam-gu, Pohang 790-784, Republic of Korea
(E-mail: ree@postech.edu)

Abstract

Rubbed films of a series of poly(*p*-phenylene 3,6-bis(4-(*n*-alkyloxy)phenyloxy)pyromellitimide)s (Cn-PMDA-PDA PIs), which are well-defined brush PIs composed of two aromatic-aliphatic bristles per repeat unit of a fully rodlike backbone, were investigated in detail using atomic force microscopy (AFM), optical retardation analysis and linearly polarized infrared (IR) spectroscopy in order to elucidate their surface morphology and molecular orientation. The liquid crystal (LC) alignment behavior and the anchoring energy of LC molecules on the rubbed films were also determined.

Introduction

Films of aromatic polyimides (PIs) are widely used as liquid crystal (LC) alignment layers in the mass-production of flat-panel LC display devices because of their advantageous properties such as excellent optical transparency, adhesion, heat resistance, dimensional stability and insulation [1]. PI film surfaces need to be rubbed with a velvet fabric to produce a uniform alignment of LC molecules with a defined range of pretilt angles.[1,2] As a consequence, much effort has been devoted to developing high performance PI materials [2,3] and to determining their LC alignment mechanism on rubbed PI film surfaces [2-6]. For most PI films reported to date, the rubbing process was found to create microgrooves along the rubbing direction and also to orient polymer main chains along the rubbing direction [2-6]. Such unidirectionally developed microgrooves and oriented polymer main chains were found to cooperatively work together to align LC molecules along the rubbing direction through their anisotropic interactions with LC molecules [2-6].

However, we first discovered new polyimides, Cn-PMDA-PDA PIs that can align LC molecules perpendicular to the rubbing direction, which is a significant departure from the LC alignment behavior typically observed for rubbed PI films. In this study we investigated the alignment properties of films of a series of poly(p-phenylene 3,6-bis(4-(n-alkyloxy)phenyloxy)-pyromellitimide)s (Cn-PMDA-PDA PIs; n = 4, 6, 7, and 8). The surface topographies of nanoscale films of these PIs were examined using atomic force microscopy (AFM), and the orientational distributions of the polymer main chains and the bristles of the PI films were characterized by optical phase retardation analysis and linearly polarized IR spectroscopy. The alignment of LC molecules in contact with rubbed PI films was investigated and, furthermore, the anchoring energies of the LCs on the films were determined. The measured alignment and anchoring energy characteristics were analyzed to elucidate the anisotropic interactions between the oriented polymer chain segments and the LC molecules. In addition, the contribution of the film surface topography to the alignment and anchoring energy was considered.

Experimental

Poly(amic acid) (PAA) precursors of Cn-PMDA-PDA PIs (Figure 1) were prepared in N-methyl-2-pyrrolidone from the respective dianhydride and p-phenylene diamine (PDA), respectively: poly(p-phenylene 3,6-bis(4-(n-hexyloxy)phenyloxy)pyromellitimide) (C6-PMDA-PDA PI), poly(p-phenylene 3,6-bis(4-(n-heptyloxy)phenyloxy)pyromellitimide) (C7-PMDA-PDA PI), C4-PMDA-PDA PI, and C8-PMDA-PDA PI.

PI films were prepared by spin casting the PAA solutions onto calcium fluoride windows for the FTIR spectra, onto gold-coated silicon wafers for the AFM images, and onto indium tin oxide (ITO) glass substrates for the optical retardation and LC cell assemblies, followed by drying on a hot plate at 80°C for 1 hr. The dried PAA precursor films were thermally imidized in an oven under dry nitrogen gas. The resulting PI films were found to have a thickness of around 200 nm, using a spectroscopic ellipsometer and an alpha-stepper. The PI films coated onto the substrates were rubbed at various rubbing densities using a laboratory rubbing machine with a roller covered with a rayon velvet fabric. The rubbing density was varied by changing the cumulative rubbing time for a constant rubbing depth, 0.37 mm.

Some of the rubbed PI films on glass substrates were cut into 2.5 cm × 2.5 cm pieces, which were then used in the assembly of LC cells as follows. Paired pieces cut from each glass substrate were assembled together antiparallel with respect to the rubbing direction by using 50 μm thick spacers, injected with a Merck nematic LC [n_e (extraordinary refractive index) = 1.5697 and n_o (ordinary refractive index) = 1.4769; Merck, USA] and then sealed with an epoxy glue, giving antiparallel nematic LC cells. In addition, a solution of the LC in ethyl ether (10 wt-% LC) was directly spin-coated onto some of the rubbed PI films, and dried at room temperature for 5 h.

Surface images were obtained with a tapping mode atomic force microscope. Optical phase retardations were measured using an optical set up equipped with either a photoelastic modulator with a fused silica head or a quarter plate. FTIR spectroscopic measurements were carried out on a FTIR spectrometer equipped with a single diamond polarizer.

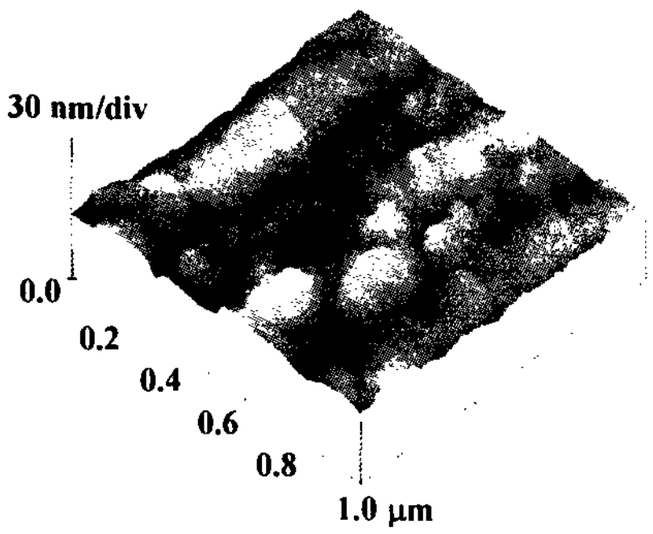

Figure 1. Typical AFM image of a rubbed Cn-PMDA-PDA PI film. The arrow indicates the rubbing direction.

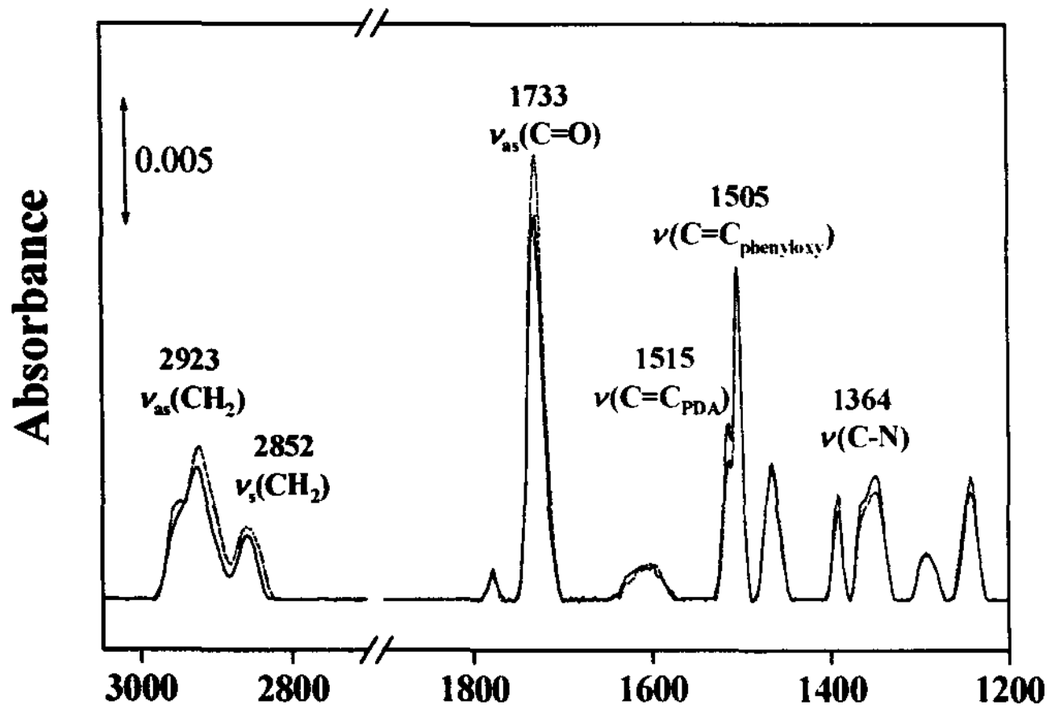

Figure 2. FTIR dichroic spectrum of a Cn-PMDA-PDA PI film rubbed with a rubbing density of 120. The solid and dashed lines are the FTIR spectra with the IR light polarized parallel to the rubbing direction and with the IR light polarized parallel perpendicular to the rubbing direction respectively.

Results and Discussion

Figure 1 shows a groove morphology developed on the PI film by rubbing process; the groove texture was developed along the rubbing direction. The characteristics of the microgrooves on the rubbed film surfaces (i.e., microgroove shape, size, and size distribution, and periodicity of microgroove lines), vary depending on the length of the *n*-alkyl bristle end group in the PI.

Figure 2 shows dichroic FTIR spectra measured for a rubbed Cn-PMDA-PDA PI film. These FTIR spectral results together with optical retardation results indicate that at the surfaces of all of the rubbed PI films, the polymer main chains and the *n*-alkyl bristle end groups were oriented along the rubbing direction, whereas the phenyloxy bristle units were oriented perpendicular to the rubbing direction.

The rubbed films of Cn-PMDA-PDA PIs (Cn: C4, C6, and C7) were found to induce LC alignment perpendicular to the rubbing direction. The unusual tendency of LC molecules to align perpendicular to the rubbing direction is driven by the favorable anisotropic interactions of LC molecules with the perpendicularly oriented phenyloxy bristle units, which override the interactions of the LC molecules with the polymer main chains, the *n*-alkyl bristle end groups, and the grooves in the film surface. However, rubbed surfaces of the C8-PMDA-PDA PI film induced LC alignment parallel to the rubbing direction, even though this PI has only one to four more carbons in the *n*-alkyl bristle end group in comparison to the other PIs.

Collectively the LC alignment, surface morphology, and polymer segmental orientation results lead a conclusion that the *n*-alkyl bristle end groups play an important role in LC alignment on rubbed Cn-PMDA-PDA PI films, and that this role is dependent on the length of the n-alkyl chain; specifically, the n-alkyl bristle end groups oriented parallel to the rubbing direction hinder perpendicular LC alignment because of their van der Waals interactions with the aliphatic tails of the LC molecules. The critical length of the n-alkyl bristle end group at which the LC alignment at the rubbed PI films changes from perpendicular to parallel is eight carbons (i.e., the n-octyl end group).

Conclusions

LC alignment on the surfaces of rubbed Cn-PMDA-PDA PI films is determined by a play-off between the directionally anisotropic interactions of the LC molecules with the oriented segments of the polymer main chains, the oriented segments of the bristles, and the microgrooves

Acknowledgements

This study was supported by the Korea Science & Engineering Foundation via the Center for Integrated Molecular Systems and by the Ministry of Education (BK21 Project).

References

[1] (a) Collings, P. J.; Patel, J. S., eds. *Handbook of Liquid Crystal Research*; Oxford University Press: Oxford, 1997. (b) Cognard, J. *Alignment of Liquid Crystals and Their Mixtures*; Gorden & Breach: London, 1982.

[2] (a) Kim, S. I.; Ree, M.; Shin, T. J.; Jung, J. C. *J. Polym. Sci.: Part A: Polym. Chem.* **1999**, *37*, 2909. (b) Park, J. H.; Jung, J. C.; Sohn, B. H.; Lee, S. W.; Ree, M. *J. Polym. Sci.: Polym. Chem.* **2001**, *39*, 3622. (c) Park, J. H.; Sohn, B. H.; Jung, J. C.; Lee, S. W.; Ree, M. *J. Polym. Sci.: Polym. Chem.* **2001**, *39*, 1800. (d) Lee, S. W.; Kim, S. I.; Park, Y. H.; Ree, M.; Lee, K. H.; Jung, J. C. *Mol. Cryst. Liquid Cryst.* **2001**, *368*, 4327. (e) Lee, S. W.; Kim, S. I.; Park, Y. H.; Ree, M.; Rim, Y. N.; Yoon, H. J.; Kim, H. C.; Kim, Y. B. *Mol. Cryst. Liquid Cryst.* **2000**, *349*, 279. (f) Kim, S. I.; Shin, T. J.; Ree, M.; Jung, J. C. *J. Soc. Inform. Display* **2000**, *8*, 61.

[3] (a) Lee, K. H.; Jung, J. C. *Polym. Bull.* **1998**, *40*, 407. (b) Lee, S. W.; Kim, S. I.; Park, Y. H.; Ree, M.; Lee, K. H.; Jung, J. C. *Mol. Cryst. Liq. Cryst.* **2000**, *349*, 271. (c) Jung, J. C.; Lee, K. H.; Sohn, B. S.; Lee, S. W.; Ree, M. *Macromol. Symp.* **2001**, *164*, 227.

[4] (a) Kim, S. I.; Pyo, S. M.; Ree, M.; Park, M.; Kim, Y. *Mol. Cryst. Liq. Cryst.* **1998**, 316, 209. (f) Lee, E. S.; Vetter, P.; Miyahita, T.; Uchida, T. *Jpn. J. Appl. Phys.* **1993**, *32*, L1339. (b) Mori, N.; Morimoto, M.; Nakamura, K. *Macromolecules* **1999**, *32*, 1488. (c) Kim, Y. B.; Olin, H.; Park, S. Y.; Choi, J. W.; Komitov, L.; Matuszczyk, M.; Lagerwall, S. T. *Appl. Phys. Lett.* **1995**, *66*, 2218. (d) Kim, Y. B.; Ban, B. S. *Liquid Crystals* **1999**, *26*, 1579.

[5] (a) Pidduck, A. J.; Bryan-Brown, G. P.; Haslam, S.; Bannister, R.; Kitely, I.; McMaster, T. J.; Boogaard, L. *J. Vac. Sci. Technol. A* **1996**, *14*, 1723. (b) Kim, J.; Kumar, S. *Phys. Rev. E* **1998**, *57*, 5644. (c) Mahajan, M. P.; Rosenblatt, C. *Appl. Phys. Lett.* **1999**, *75*, 3623.

[6] (a) Nazarenko, V. G.; Lavrentovich, O. D. *Phys. Rev. E.* **1994**, *49*, R990. (b) Durand, G. *Physica A* **1990**, *163*, 94. (c) Barbero, G.; Evangelista, L. R.; Madhusudana, N. V. *Eur. Phys. J.* **1998**, *1*, 327.