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Quantitative Analysis on Polymer Segmental Orientations and Surface Topography in Rubbed and Photoreacted Polyimide Films and Their Interactions with Liquid Crystal Molecules

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A series of poly(*p*-phenylene 3,6-bis(4-(*n*-alkyloxy)phenyloxy)pyromellitimide)s (C_n-PMDA-PDA PIs) with various lengths of the *n*-alkyl bristle end group, which are well-defined polymer rods with two bristles per repeat unit of the polymer rod backbone, were studied as thin films using atomic force microscopy, optical retardation, and linearly polarized infrared spectroscopy before and after rubbing with a velvet fabric, and their nematic liquid crystal (LC) aligning abilities were investigated. The LC molecules on the rubbed film surfaces of C_n-PMDA-PDA PIs with *n*-butyl, *n*-hexyl, and *n*-heptyl bristle end groups were found to be aligned perpendicular to the rubbing direction; this is a significant departure from the parallel LC alignment observed for all conventional PI materials. In contrast, rubbing of the film surfaces of C_n-PMDA-PDA PI with *n*-octyl bristle end groups induced LC alignment parallel to the rubbing direction. Both the perpendicular and parallel LC alignments were determined to have very large anchoring energies ($> 1 \times 10^{-3}$ J/cm²). The rubbing process was found to create microgrooves in the PI films along the rubbing direction, and to orient the polymer main chains and the *n*-alkyl bristle end groups along the rubbing direction, but to orient the phenyloxy bristle units perpendicular to the rubbing direction. These results collectively indicate that the *n*-alkyl bristle end groups play an important role in LC alignment, and that this role depends on the length of the *n*-alkyl chain; specifically, the parallel oriented *n*-alkyl bristle end groups 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 for the transition from perpendicular to parallel LC alignment at the rubbed PI films is eight carbons (i.e., the *n*-octyl end group). In conclusion, LC alignment on the surfaces of rubbed PI films is determined by a play-off between the directionally anisotropic interactions between the LC molecules and (i) the

oriented segments of the polymer main chains, (ii) the oriented segments of the bristles, and (iii) the microgrooves.

In addition to the rubbing type of PIs above, photoreactive polyimide (PSPI) with cinnamate (CI) chromophore and its derivatives as side groups that forms good quality films through conventional solution spin-casting and drying processes was successfully synthesized with a reasonably high molecular weight. Among the synthesized PSPIs, a representative PSPI is poly(3,3'-bis(cinnamoyloxy)-4,4'-biphenylene hexafluoroisopropylidenedipthalimide) (6F-HAB-CI). This 6F-HAB-CI PSPI is thermally stable up to 340°C, its glass transition temperature (T_g) is 181°C, and it was determined by prism coupling to be positively birefringent. The photochemical reactions of the PSPI in solution and in films, as well as the molecular orientations of the PSPI that are induced by exposure of its films to linearly polarized ultraviolet light (LPUVL), were investigated in detail by nuclear magnetic resonance, ultraviolet-visible, infrared, and Raman spectroscopies, and by dissolution testing and optical retardation measurements. It was confirmed that the CI chromophores of the PSPI undergo both photoisomerization and photodimerization. LPUVL exposure was found to induce anisotropic orientations of the polymer main chains and of the CI side groups in the films. Moreover, the LPUVL-irradiated films homogeneously aligned nematic liquid crystal (LC) molecules along a direction at an angle of 107° with respect to the polarization of the LPUVL, which coincides with the orientation direction of the PSPI polymer chains. This result shows that the LC alignment process is principally governed in irradiated PSPI films by the orientations of the polymer main chains and the unreacted CI side groups. Along the director of the LC alignment in the cell, the pretilt angle was measured to be 0–0.15°, depending on the exposure energy and the exposure method. The LC alignment was found to be thermally stable up to 200°C, which is 20°C higher than the T_g of the film. In summary, the LC alignment characteristics of the 6F-HAB-CI PSPI make it a promising candidate material for use as the LC alignment layer in advanced LC display devices with in-plane switching modes that require as low as possible LC pretilt angles.

Further, the mechanisms of polymer segmental orientations at the PI film surface due to the rubbing process as well as the LPUVL exposure were investigated in detail. The results are discussed with considering all related factors.