

別紙様式 8

研 究 主 論 文 抄 録

論文題目 Thermal and photo-induced alignment behavior of polyethylene imines  
having azobenzene side chain groups

(アゾベンゼン側鎖を有するポリエチレンイミンの熱的および光化学的配向挙動)

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主論文要旨

《本文》

Azobenzene containing polymers have been the object of intensive investigations because of their potential applications in the field of photonics and optoelectronics. Under irradiation with an appropriate wavelength of light the azobenzene moieties change their spatial orientation and in this way anisotropy – dichroism and birefringence – is generated. It was also reported that some polyethylene imines (PEIs) having azobenzene groups as side groups show liquid crystalline phases and align perpendicular direction to the substrate spontaneously by heating into an isotropic phase and following cooling without any alignment process. So the goal of this research was to synthesize new class of PEIs having azobenzene side chain group and thermally and photochemically control the molecular orientation of PEIs between random state and out-of-plane structures to fabricate the optical switching system showing excellent memory stability. Therefore, the synthesis of PEIs having different substituent groups and different methylene spacer group and their thermal and photo alignment behavior were elaborately investigated. In the following section, the on-off photo switching behavior of PEIs and PVA multiply layered films is also described.

In 2<sup>nd</sup> chapter of my thesis, I described preliminary study on the fabrication of new light driven polymeric actuator based on multi-layered films of poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] and molecular alignment behavior of azobenzene polymer. Multi-layered films showed very little bending and unbending properties upon UV-laser and visible light (435 nm) irradiation respectively and also showed very little out-of-plane ordering on annealing. So after that I changed my topics and choose PEIs for studying molecular alignment behavior.

In Chapter 3, synthesis, thermal and photo alignment behavior of PEIs having different substituent (-CN, -C<sub>4</sub>H<sub>9</sub>, -OCH<sub>3</sub> and -NO<sub>2</sub>) azobenzene side chain group with six methylene spacer is described. Synthesized PEIs were characterized by DSC, Polarized Optical Microscopic and XRD analysis. All polymers showed liquid crystalline (LC) properties. Spin coated films of PEIs showed the out-of-plane molecular orientation on annealing. Except PEI6N from -NO<sub>2</sub> substituent group, all PEIs showed reversible alignment behavior on annealing, UV and non polarized visible light irradiation. The results indicated that the molecular orientation behavior of polyethylene imines significantly depends on the structure of the azobenzene side chain groups.

In 4<sup>th</sup> Chapter, I described the elaborate study on synthesis, thermal and photo alignment behavior of PEIs having nitro (-NO<sub>2</sub>) substituent azobenzene side chain group with different methylene spacer. All synthesized polyethylene imines (PEImN) showed LC properties and the melting temperatures of polymers showed an odd-even effect. PEImN spin coated films exhibited out-of-plane orientational behavior on annealing and ordering behavior significantly dependent on spacer length. Because of the presence of both electron-donating and electron-withdrawing substituents at both ends of azobenzene group, PEImN showed very little photo alignment ordering.

Comprehensive study on synthesis and multiple reorientational behaviors of PEIs having methoxy (-OCH<sub>3</sub>) substituent azobenzene side chain group with different methylene spacer groups (PEImM) are described in chapter 5. PEImM films showed out-of-plane molecular ordering of azobenzene chromophores on annealing and non-polarized visible light irradiation. PEImM films also exhibited reversible molecular orientation from random state to out-of-plane and from out-of-plane to random state on annealing, non-polarized UV and visible light irradiation. The reversible molecular ordering of PEImM films was greatly dependent on the spacer length.

In Chapter 6, a comparative study of on-off photo switching behavior of multiply layered films of PEIs having different substituent azobenzene side chain groups and PVA is described in details. PEI6M-PVA multiply layered films showed reversible structural color on annealing and UV light irradiation. But PEI6N only showed structural color change on annealing. PEI6C and PEI64 did not show such type of structural color. The color reflectance of multiply layered films could be tuned by changing the orientation of azobenzene groups followed by the change in refractive index of azobenzene polymer layers by the trans-cis photoisomerization upon irradiation of UV/visible light.

Finally in last chapter, the results are summarized.