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Optically Induced Anisotropy of Polyurethane Containing Heterocyclic Azo Chromophores

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We synthesized two different polyurethanes containing methylsulfonyl benzothiazolyl azo chromophore (MS-polyurethane) and p-nitroazobenzene chromophore (NP-polyurethane) in the side chain by condensation polymerization respectively. The structural effect of the chromophore on the level and the induction rate of induced birefringence was investigated. Polarized absorption spectroscopy was employed to study the reorientation of azobenzene chromophore using two polymers. We also investigated the properties of optically induced birefringence in polyurethane film by changing the wavelength ($\lambda = 488$ nm, 514 nm) of the linearly polarized excitation light.

Keywords: optical anisotropy, azobenzene chromophore, polyurethane

INTRODUCTION

There has been great interest in the synthesis and characterization of azobenzene containing polymers for several reasons as these materials to possess unique optical properties. The main interest of these systems is the induction of optically induced anisotropy when they are irradiated with linearly polarized light. This is a very promising property for optical

information storage and erasing. Several researchers have recently performed a number of studies on how structural factors affect the dynamics of the photo-induced orientation of azobenzene moiety^[1-2].

In an attempt to investigate the structural effect of the chromophore, we designed and synthesized two polymers containing different chromophores in the side chain. Using two polymers, we investigated the properties of optically induced birefringence and induction rate in polyurethane film by changing the wavelength ($\lambda = 488\text{nm}$, 514nm) of the excitation light. Additionally, polarized absorption spectroscopy was employed to study the reorientation of azo chromophore.

EXPERIMENTAL

The structures of polymers were illustrated in Figure 1. The film was spun on normal glass slide after filtering the solution with an acrodisc filter. The change in transmission of the He-Ne laser through the film between crossed polarizers is recorded as a function of time under irradiation of a linearly polarized light. Angular-dependent absorbance

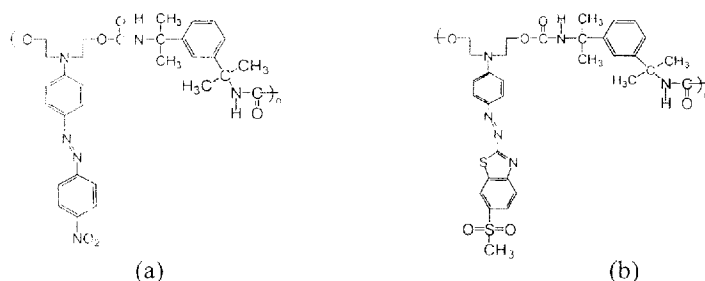


FIGURE 1 Structures of polymers. (a) NP-polyurethane; (b) MS-polyurethane

of two polymers were measured by using polarized UV/VIS spectroscopy.

RESULTS AND DISCUSSION

Photo-induced *trans-cis* isomerization in azobenzene and its derivatives is a well-known process. Aminoazobenzene type molecules are characterized spectroscopically by a close proximity of $n-\pi^*$ and $\pi-\pi^*$ bands; the former is frequently buried beneath the intense $\pi-\pi^*$ absorption band. [3] Two absorption spectra of the polymers were shown

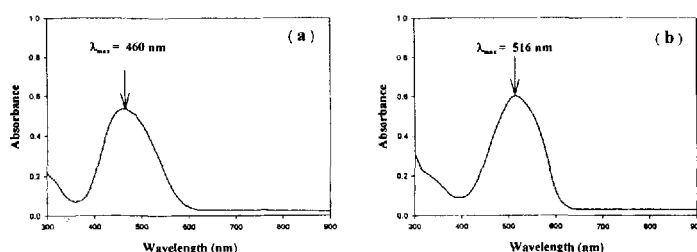


FIGURE 2 The absorption spectra of the film of polyurethanes.(a) NP-polyurethane; (b) MS-polyurethane

in Figure 2. The present work describes the structural effect of the chromophore on the level of the induced birefringence and the induction rate. In order to study the effect of the chromophore, we investigated the properties of optically induced birefringence in polymer film by changing the wavelength ($\lambda = 488\text{nm}$, 514nm) of the pumped light. The variation of the photo-induced signal is depicted in Figure 3.

This indicates that the induction of anisotropy is faster in NP-polyurethane. The birefringence would depend on the quantum yield, the *trans-cis-trans* isomerization rates, and the local mobility of azo moiety.

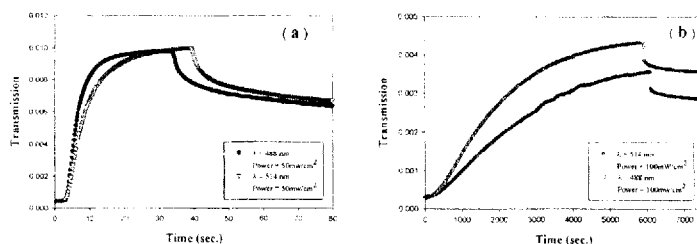


FIGURE 3 Growth and decay process of photo-induced transmission on polyurethane film; (a) NP-polyurethane; (b) MS-polyurethane

*Pump beam intensity (50 and 100 mW/cm²); wavelength ($\lambda = 488$ and 514 nm)

In MS-polyurethane, the bulkiness of diazo component in the chromophore is much higher so that the mobility of azobenzene could be much reduced. Although the absorption coefficient at the wavelength of the pump beam is larger, the rate of inducing optical anisotropy is smaller due to the bulkiness of the azobenzene chromophore. The results described in this work provide an approach for the structural design of azobenzene moiety and choice of pump beam that can show fast induction rate and the high level of the birefringence.

References

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