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Photochromism of Liquid Crystalline Polymers with Spiropyran Derivatives

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Abstract New liquid crystalline polymers with spiropyran derivative for optical recording applications were prepared by radical polymerization from two different monomers composed of mesogenic unit and spiropyran moiety. The resulting polymers have been characterized by FT-IR, ^{1}H-NMR, DSC and UV/Vis spectroscopy. The weight average molecular weight (M_w) of polymers were in the range of 13,000-30,700 and thermal decomposition initiated in the range of 350-370 °C. Good quality films were obtained by spin-coating onto indium tin oxide (ITO) glass plate and some of polymers exhibited smectic and nematic liquid crystalline phase at elevated temperatures. These polymers showed promising photochromic and thermochromic activities for optical recording materials.

INTRODUCTION

Novel photo-active materials and systems are required for much faster recording or switching and higher storage density, as the speed of computers is getting faster and the volume of information expands rapidly. Photon-mode recording or switching based on changes in absorption and/or refractive index by photo-reactions is expected to have many advantages as compared to heat-mode recording, magnetic recording, or electro-optic switching [1]. Various photochromic systems have recently attracted much interest in view of their promising applicability to high-speed and high-density photon-mode optical memory. The photochromism reported so far involves changes of

chemical bonds such as ring opening and closing or cis-trans isomerization [2]. One of the most important classes of photochromic materials is spiropyran derivatives [3,4]. Upon irradiation with UV light the spiropyran which is a typical photochromic compound undergoes heterolytic cleavage of the carbon-oxygen bond to form colored isomers. A reversal transformation from colored to colorless spiropyran immediately occurs upon exposure to thermal or photochemical energy.

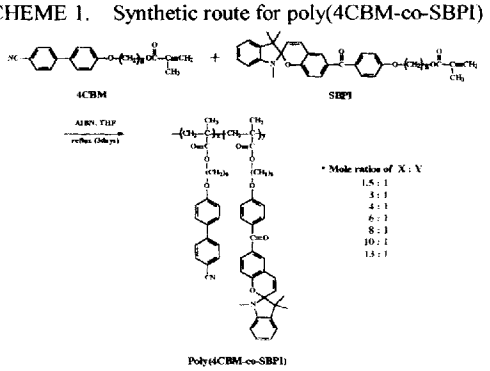
Recently we have focused our attention to liquid crystalline polymers with spiropyran derivatives for optical recording applications. In this paper, we report the synthesis and photochromism effects of these polymers.

EXPERIMENTAL

Synthesis of Polymers

Two different vinyl monomers consisting of mesogenic unit and spiropyran moiety in 1 wt.% of AIBN in THF were refluxed under a nitrogen atmosphere for 72 h. After cooling to room temperature, the solution was precipitated into methanol and then filtered. The products were dried under vacuum at the elevated temperature and the resulting polymers are shown in Scheme 1 for various mole ratio of mesogenic unit and spiropyran moiety.

SCHEME 1. Synthetic route for poly(4CBM-co-SBPI)



RESULTS AND DICUSSION

The photoactive polymers were obtained by radical copolymerization from two different vinyl monomers composed of mesogenic and spiropyran units. The resulting polymers have been characterized by

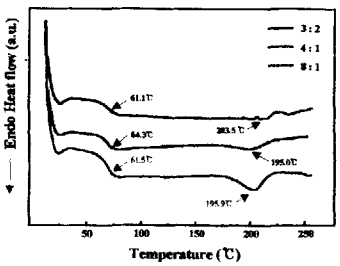
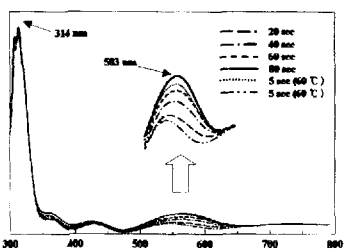
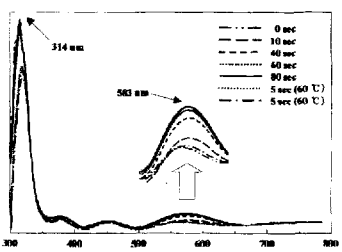


FIGURE 1 DSC curves of poly(4CBM-co-SPBI) series



Mole ratio of 4CBM:SBPI = 3:1

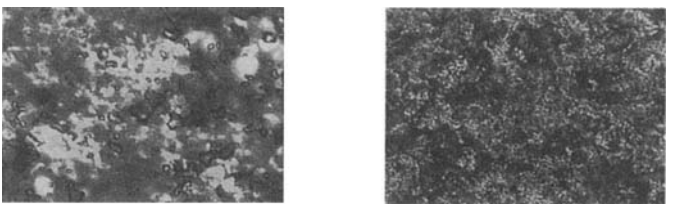


Mole ratio of 4CBM:SBPI = 8:1

FIGURE 2. UV-vis spectra of poly(4CBM-co-SBPI) with different compositions of mesogenic and spiropyran units

FT-IR, ^{1}H-NMR, and elemental analysis. The weight average molecular weights (M_w) were determined to be 13,300-30,700 (M_w/M_n =1.6-2.6) by gel chromatography using polystyrene as standard. Their glass transition temperatures appeared between 54-65 °C, depending on the monomer composition ratio. Analysis by polarizing microscopy indicated the formation of a smectic phase on heating or cooling of poly(4CBM-co-SBPI). Some of polymers exhibited smectic and

nematic liquid crystalline phase at 108 °C and 157 °C (Fig. 3), respectively. All of polymers presented photochromic and thermochromic activities required for optical recording materials. As shown Figure 2, absorbance from the ring-opened merocyanine of the spiropyran is clearly dependent on UV irradiation time. The photostationary state of poly(4CBM-co-SPBI) films can be observed after UV irradiation for 80 sec at room temperature. By heat treatment or under visible light, the intensity of the peak about positioned at 580 nm disappears due to the thermochromic effect of merocyanine.



(a) (b)

FIGURE 3. Polarized Optical Microscopy Images of poly(4CBM-co- SBPI) (8 : 1) (a) 108 °C (b) 157 °C

ACKNOWLEDGEMENT

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