

Note

PHOTOINDUCED ALIGNMENT OF OPTICALLY ACTIVE POLYMER CONTAINING A TEMPO RADICAL END GROUP*

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Abstract A new azobenzene side-chain polymer (TEMPO-PAZ) containing TEMPO (4-hydroxy-2,2,6,6-tetramethylpiperidinoxy) radical end group was synthesized by free radical copolymerization. Photoinduced alignment was studied on the polymer films at room temperature with linearly polarized light of 514.5 nm. The experimental results showed that the magnetic response intensity of the TEMPO-PAZ could be easily controlled by choosing the appropriate polarized light irradiating times, presumably due to the nitroxide radical in the TEMPO-PAZ molecular structure. For the polymer investigated here, the photoinduced alignment technique was introduced to increase the magnetic response intensity of polymer under irradiation, aiming originally at searching for a new photo-active organic magnetic multifunctional materials. On the other hand, experimental results also showed that the TEMPO-PAZ can be used as a material for optical image storage.

Keywords Azobenzene nitroxide radical polymer, Photo-active organic magnetic materials, Photoinduced alignment

INTRODUCTION

Recently great attention has been paid to the investigation of the photoinduced optical anisotropy in liquid crystalline side chain polymers with azo-chromophores chemically attached to a polymer chain^[1, 2]. Polymers containing aromatic azo units have been used in various research fields^[3–8]. In fact, this photoisomerization of the azobenzenes in a polymer and its related property changes are being actively explored for potential applications, such as in optical switching and optical information storage^[9–12]. Such a photo-induced geometrical or conformational change can significantly influence the bulk and surface properties of the polymer^[7, 8]. Recently, we find great interest in the increasing magnetic response intensity of the azobenzene side-chain polymer containing a TEMPO radical end group on use of the photoinduced alignment technique.

In our previous work, we have synthesized a series of polymers functionalized with aromatic azo groups for the study of their photoinduced holographic phase gratings^[13, 14]. In this paper, an attempt has been made to study the influence of azobenzene side-chain polymer containing a TEMPO (4-hydroxy-2,2,6,6-tetramethylpiperidinoxy) radical on optic-magnetic characteristics. For the polymer studied here, we introduced the TEMPO radical end group to increase the magnetic response intensity with linearly polarized light in order to find a new kind of organic magnetic multifunctional material. An investigation of magnetic response intensity change of side-chain azobenzene polymer films with TEMPO radical end group on linearly polarized light irradiation and the evaluation of their optical characteristic are described here.

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EXPERIMENTAL

Materials

The chemical structure of the azobenzene side-chain polymer (TEMPO-PAZ) containing a TEMPO radical end group is shown in Fig. 1. The detailed synthesis and structure characterization of the TEMPO-PAZ were reported elsewhere^[14]. The azobenzene side-chain polymer (TEMPO-PAZ) containing a TEMPO radical end group was prepared by the reaction of the polymer PAZ with the TEMPO radical in THF. Elemental analysis of TEMPO-PAZ was shown to have 83% of the carboxy groups esterified.

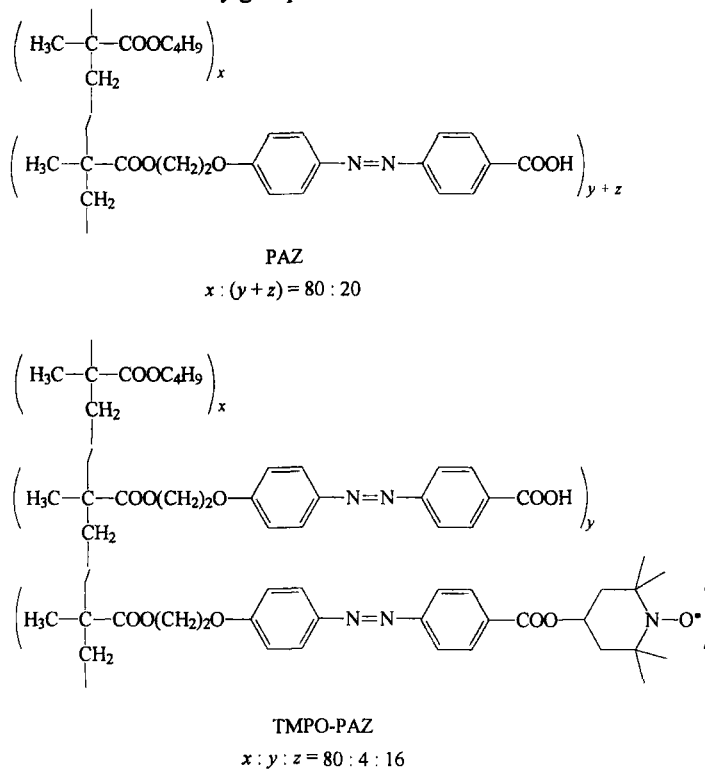


Fig. 1 The molecular structures of the polymers

Preparation of Polymer Film

The homogeneous solution of newly synthesized polymer in spectroscopic grade THF was filtered through 0.2 μm membranes. The solution was spin-coated onto glass slides. The film thickness was controlled to 0.5–2 μm by adjusting the solution concentration and the spin speed. The film thickness was measured by using atomic force microscopy (AFM). The spin-coated films were dried under vacuum for 24 h at 50°C, and were stored in a desiccator for further measurements^[13, 14].

Formation of Photoinduced Holographic Grating

The experimental setup for the grating formation has been reported elsewhere^[13–15]. A linearly polarized laser beam at 514.5 nm from an Ar^+ laser was used as the recording source. The polarized laser beam passes through a halfwave plate, and is then expanded and collimated. The polarization condition of the recording beam can be adjusted by rotating the halfwave plate. The grating spacing depends on the period of interference pattern, which can be adjusted by changing the angle (2θ) between the two writing beams.

RESULTS AND DISCUSSION

Polymer Photoprocessing

Spin coated thin films of newly synthesized azo polymer was used to carry out the photoprocessing experiments.

The experimental at setup and recording conditions have been previously reported^[13, 14] and also described briefly in the experimental part of this paper.

Magnetic Properties

The ESR spectra of benzene show three absorption lines with $g = 2.0060$ and $a_N = 15.5$ G for TEMPO-PAZ^[14]. Temperature dependence of the magnetic susceptibility of TEMPO-PAZ was investigated with a SQUID magnetometer and a MagLab 2000 system at 2–300 K. Figure 2 shows the plot of χ versus T ; χ being the molar magnetic susceptibility and T the temperature for TEMPO-PAZ. As shown in Fig. 2, when the temperature is lowered from 40 K down to 2 K, χ increases very rapidly. This behaviour is characteristic for intermolecular antiferromagnetic interactions. On the other hand, it was found that after irradiation with linearly polarized light, the polarized light creates much stronger magnetic response intensity of the TEMPO-PAZ than that of a TEMPO-PAZ without treatment by polarized light irradiation. It can be seen from Fig. 3 that curve D corresponding to magnetic response intensity is almost 2 times higher than curve B without light irradiation treatment of the polymer. Actually, these results clearly indicate that after polarized light irradiation, the molecules in TEMPO-PAZ film are reoriented regularly.

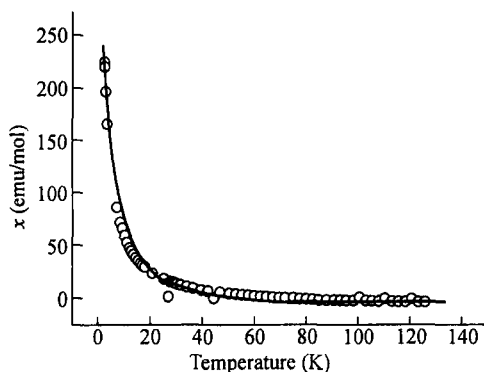


Fig. 2 Temperature dependence of magnetic susceptibility for the TEMPO-PAZ

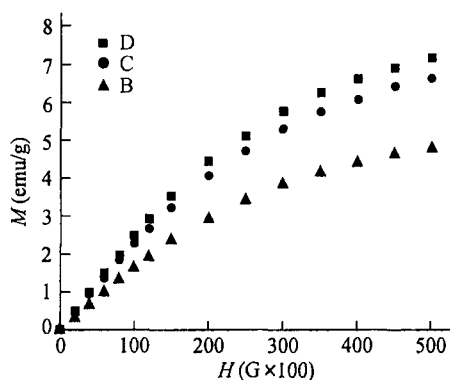


Fig. 3 Magnetic field intensity dependence of magnetic susceptibility for the TEMPO-PAZ at 5 K ($\lambda = 514.5$ nm)

B: not exposed to polarized light, C: exposed to one polarized light, D: exposed to three polarized light

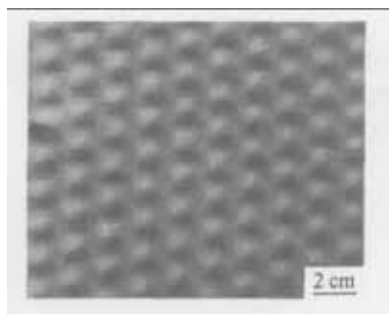


Fig. 4 The POM image of TEMPO-PAZ film exposed to three polarized light
Hexagonal symmetry optical lattice

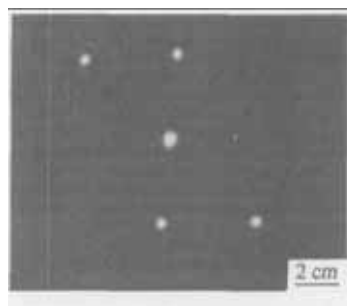


Fig. 5 The first-order diffraction pattern of a He-Ne laser beam for the TEMPO-PAZ film

Holographic Grating Recording

The holographic grating of TEMPO-PAZ film was investigated by the degenerate four-wave mixing (DFWM) AFM^[13–15]. However, surface gratings could not be observed for TEMPO-PAZ film containing azobenzene with carboxy group due to the strong intermolecular interactions. After irradiation, however, resolution of the stored

image can be examined under the polarizing microscope. As shown in Fig. 4, a clear photoimage with good resolution was obtained. On the other hand, we note that, once recorded, the image is stable under ambient conditions at least for weeks. It is of great importance, moreover, that the holographic grating can be read out by polarized He-Ne laser. Figure 5 shows the reading out image of the film recorded under ambient conditions with 633 nm polarized light. These results reveal that TEMPO-PAZ can be used as materials for optical image storage.

CONCLUSION

In summary, we have demonstrated that the alignment change was induced in TEMPO-PAZ film, and the magnetic response intensity could be easily controlled by choosing the appropriate polarized light irradiating times. Experimental results also showed that the TEMPO-PAZ can be used as a material for optical image storage.

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