

Rapid Communication

SYNTHESIS AND PROPERTIES OF A NEW AZOBENZENE SIDE-CHAIN
POLYMER CONTAINING A TEMPO RADICAL*

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Abstract To allow anisotropies of optical properties in a magnetic field, nitroxide radical is introduced into the *ortho*-position of the phenylene ring in the side chain. A new azobenzene side-chain polymer (TEMPO-PAZ) containing TEMPO radical was synthesized. The polymer has a good solubility in organic solvents. The ESR spectrum of the polymer indicated three absorption lines characteristic of TEMPO radical. The optical phase conjugated responses (I_4) of the polymer films were investigated by degenerate four-wave mixing (DFWM). The experimental results showed that optical phase conjugated response of the TEMPO-PAZ could be easily controlled by choosing the appropriate direction of magnetic field presumably due to the nitroxide radical in the TEMPO-PAZ molecular structure. For the polymer investigated here, the nitroxide radical was introduced to increase optical phase conjugated response intensity in a magnetic field, aiming originally at searching for a new photo-active organic magnetic multifunctional materials.

Keywords Azobenzene nitroxide radical polymer, Photo-active organic magnetic materials, Optical phase conjugated responses

INTRODUCTION

Azobenzene polymer is one of the most promising polymers for photo-induced gratings because of its reversible optical data recording and storage^[1–3]. In the previous work, we synthesized a series of novel azobenzene side-chain polymers with a chiral group (*s*-2-methyl-butyl) and elucidated their structure and physical properties such as optical properties as well as the photo-induced holographic phase gratings^[4]. On the other hand, azobenzene polymer with nitroxide radical exhibiting a wide range of magnetic properties should also enhance its solubility and processability, and even modify its properties. From the viewpoint of controlling molecular orientation, azobenzene polymers have been studied by a number of groups^[4–6]. However, there has been no report on side-chain azobenzene polymer containing nitroxide radical till now. Here, we report the synthesis and characterization of a new side-chain azobenzene polymer with nitroxide radical (TEMPO-PAZ) and the evaluation of its optical phase conjugated response in a magnetic field.

EXPERIMENTAL

Reagents

Tetrahydrofuran (THF) was purified by refluxing and distilling from calcium hydride. All of solvents and reagents, of analytical-grade quality, were commercial products and used as received unless otherwise stated.

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THF solutions into methanol. After filtration and vacuum drying, an orange colored solid polymer was obtained. The yield of polymerization reaction ranged between 56%–70%. The structure of the polymers shown was consistent with ^1H -NMR spectroscopic data. After the polymerization was complete, the vinyl proton peaks of the monomer in the methacrylic group at δ 5.5 0 and δ 6.15 had completely disappeared. Anal. Calcd for PAZ (%): C 66.72; H 7.89; N 2.94. Found: C 66.37; H 8.03; N 3.03.

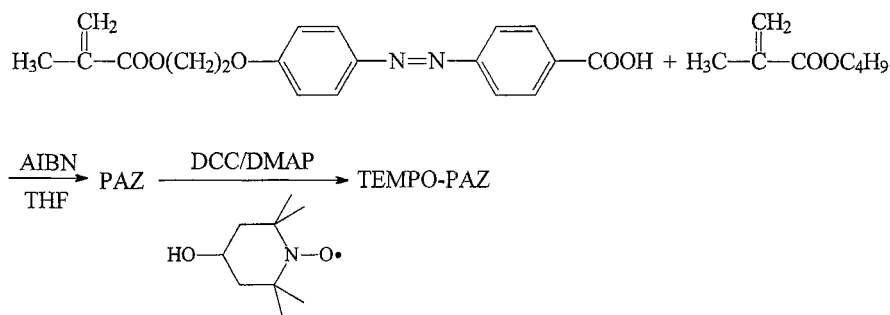


Fig. 2 The synthesis route for the polymer TEMPO-PAZ

Polymer TEMPO-PAZ

20 mmol of TEMPO, 15 mmol of PAZ, 9 mmol DMAP (4-Dimethylaminopyridine) were dissolved in 60 mL of THF. At 0°C 18 mmol of DCC (*N,N'*-dicyclohexylcarbodiimide) was added and the mixture was stirred for 30 min; a precipitate was formed. The mixture was allowed to warm to room temperature and stirred for another 18 h. The precipitate was filtered off and washed twice with solvent. The filtrate was evaporated under vacuum and purified by several reprecipitations from THF solutions into methanol. The yield of TEMPO-PAZ as a yellowish powder after filtration and vacuum drying was 87%. Anal. Calcd for TEMPO-PAZ (%): C 67.04; H 8.29; N, 3.75. Found (%): C 66.83; H 8.31; N 3.64.

RESULTS AND DISCUSSION

Synthesis of Polymers

The preparation of the TEMPO-PAZ is outlined in detail in Fig. 2. The resulting TEMPO-PAZ and PAZ were quite soluble in common organic solvents such as tetrahydrofuran and chloroform. Table 1 shows molecular weights and molecular weight distributions (MWD) of the polymers determined by GPC according to polystyrene standard. As reported in Table 1, the polydispersity indexes of the obtained polymer TEMPO-PAZ and PAZ are in the range usually observed for the radical polymerization process.

Table 1. Molecular weights and molecular weight distribution (MWD) of the polymers

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w / \bar{M}_n$
PAZ	34,000	44,000	1.3
TEMPO-PAZ	56,000	90,000	1.6

Magnetic Properties

As seen from the ESR spectrum shown in Fig. 3, side-chain azobenzene polymer containing nitroxide radical (TEMPO-PAZ) shows three absorption lines ($g = 2.0060$, $a_N = 15.5$ G) in benzene. This indicates that there are obvious characteristics of the TEMPO radical in the polymer TEMPO-PAZ. Figure 4 shows temperature dependencies of magnetic susceptibilities for TEMPO-PAZ measured in the range of 2–300 K at 3T field by magnetometer and MagLab 2000 system. As shown in Fig. 4, when the temperature decreases, magnetic susceptibilities first increases slowly, reaching a maximum around 2.3 K. Preliminary magnetic measurement suggests a paramagnetic behaviour.

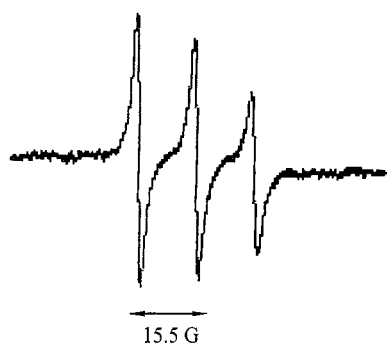


Fig. 3 ESR spectrum of the polymer TEMPO-PAZ in benzene

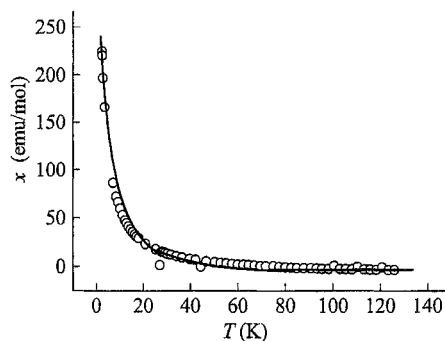


Fig. 4 Temperature dependencies of magnetic susceptibilities for the polymer TEMPO-PAZ. Solid lines show the best fit of the data.

Optical Phase Conjugated Characteristics

For the optical studies, thin polymer films were prepared by casting on the clear surface of glass or newly cleaved mica plate. For this purpose appropriate amounts of polymers were dissolved in freshly distilled THF. The solution was filtered through a $0.45\ \mu\text{m}$ Teflon filter to remove insoluble particles. It was then cast, depending on the desired thickness, onto glass or mica plate. Residual solvent was removed by heating the films at 35°C for 3 h under an external magnetic field of 9300 G. Then the optical phase conjugated characteristics measurements were performed on films with laser beam ($514.5\ \text{nm}$) as light source, and recorded with a digital storage oscilloscope. Figure 5 shows the relationship between optical phase conjugated response (I_4) and the direction of magnetic field. Here, a and c refer to the film perpendicular and parallel to an external magnetic field, respectively. From Fig. 5, we note that I_4 of TEMPO-PAZ film depends strongly on the direction of magnetic field. Since the nitroxide radical in the polymer film should have a larger orientational power than the azobenzene moieties, it would be preferentially aligned parallel to an external magnetic field in advance. As a result, the optical phase conjugated response (I_4) of TEMPO-PAZ is maximized perpendicular to the magnetic field. The response model of nitroxide radical in TEMPO-PAZ film on the direction of magnetic field is shown in Fig. 6. On the other hand, in order to compare optical phase conjugated characteristics of different polymers, we adopted the polymer PAZ containing no nitroxide radical for comparison. In fact, for the same experimental condition I_4 of PAZ film (Fig. 7) was in opposition to (I_4) of TEMPO-PAZ film, presumably due to the nitroxide radical in the TEMPO-PAZ film. Further studies on the mechanism of this spontaneous behavior are in progress.

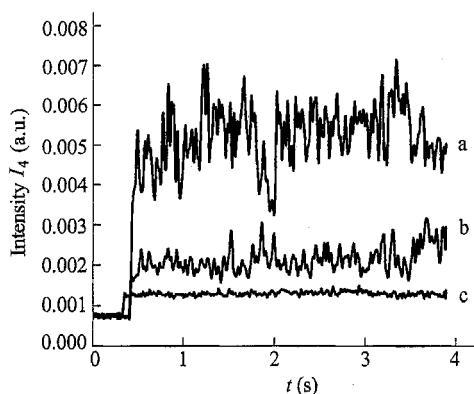


Fig. 5 Influence of the direction of magnetic field on the optical phase conjugated response (I_4) of the polymer TEMPO-PAZ
a) Film perpendicular to an external magnetic field; b) Film without using external magnetic field; c) Film parallel to an external magnetic field

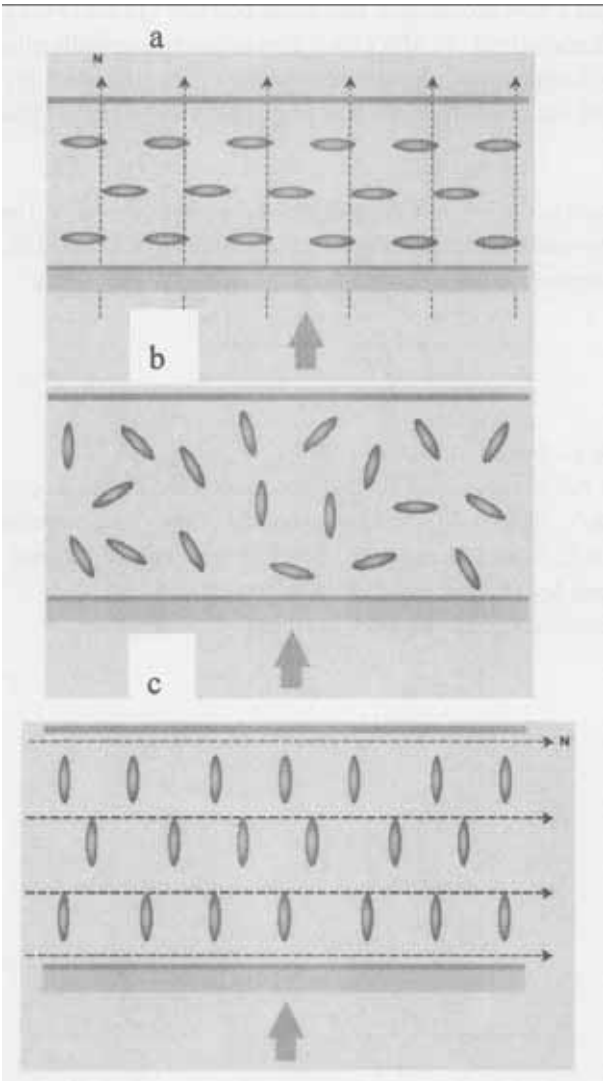


Fig. 6 The response model of nitroxide radical in TEMPO-PAZ film in the direction of magnetic field

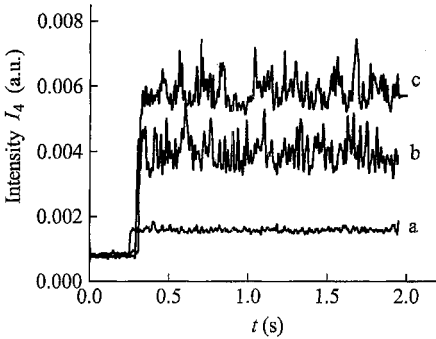


Fig. 7 Influence of the direction of magnetic field on the optical phase conjugated response (I_4) of the polymer PAZ
a) Film perpendicular to an external magnetic field; b) Film without using external magnetic field; c) Film parallel to an external magnetic field

Finally, we conclude that a new azobenzene side-chain polymer (TEMPO-PAZ) containing TEMPO radical has been synthesized and characterized. TEMPO-PAZ film is macroscopically aligned in a magnetic field. The nitroxide radical in side-chain azobenzene polymer films plays an important role in responding to the direction of the magnetic field, and can be used to change physical properties such as optical phase conjugated characteristics (I_4) effectively.

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