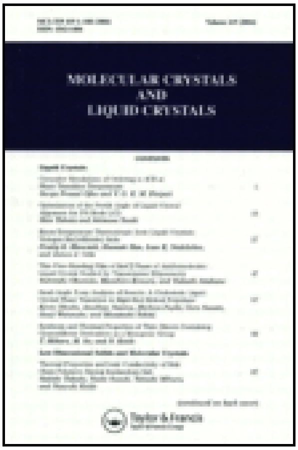

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Syntheses and Optical Properties of Polyethers with Azobenzene-Type Main Chain

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Syntheses and Optical Properties of Polyethers with Azobenzene-Type Main Chain

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Polyethers (ABPE*n*, *n*=6 and 12) were synthesized by the polycondensation reaction of 2,2′-dihydroxyazobenzene and α,ω-dichloro alkane in the presence of a phase transfer catalyst. ABPE6 and ABPE12 had the average molecular weight (M_w) of 49,000 and 67,000, and the glass transition temperature (T_g) of 112 °C and 110 °C, respectively. UV absorption spectrum of ABPE6 showed two absorption peaks with maxima at 370 nm and at 470 nm. Fluorescence emission spectrum of ABPE6 showed a peak with maximum at 669 nm.

Keywords: azobenzene; polyether; optical properties; phase transfer catalyst; polycondensation reaction

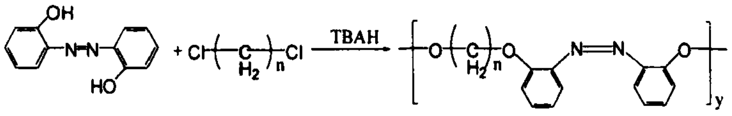
INTRODUCTION

In recent years, there have been increasing interest in the synthesis of various polymers with optical properties[1]. Polymers containing azobenzene groups have potentially photofunctional applications such as photon-mode optical memories[2], transducing optical information and photoswitching of electron conductivity, and have thus received a lot of attention. The azobenzene linkages can be incorporated into the backbone of the polymer or in the side chain[3]. A number of researchers have investigated the trans-cis photoisomerzation of the azobenzene group in the side chain of the polymer[4]. Several attempts have also been made to incorporate azobenzene units in the polymeric main chain[5]. Kumar et al. prepared polyureas containing azobenzene groups in their main chain and investigated the trans-cis photoisomerzation of these materials[6].

The objectives of this research are to prepare polyethers containing azobenzene units in the main chain via the polycondensation reaction using a phase transfer catalyst, and to investigate optical properties of the polyethers. In addition, the structurally similar polyethers, ABPE6 and ABPE12, were synthesized to compare the optical properties of polyethers with different length of the flexible spacer.

EXPERIMENTAL

1,6-dichlorohexane (10 mmol) in *o*-dichlorobenzene (20 ml) was added to a solution of 2,2'-dihydroxyazobenzene (10 mmol) and tetrabutyl ammonium hydrogen sulfate (TBAH) as a phase transfer catalyst (4 mmol) dissolved in 10*N* NaOH under nitrogen atmosphere. The reaction mixture was vigorously stirred at 70℃ for 12h. Then, the organic layer was extracted with chloroform and the combined organic extracts were poured into methanol. The precipitate was filtered, washed with water, and methanol. Finally, the polymer was dried under vacuum at 80℃ for 24h. ABPE12 was synthesized according to the previously described procedure for ABPE6, except 1,12-dichlorododecane. The reaction path to the formation of ABPE6 and ABPE12 is shown in Figure 1. The ABPE6 and ABPE12 were identified by FTIR



ABPE*n* (*n* = 6, 12)

FIGURE 1 Synthetic route of ABPE*n* (*n* = 6, 12).

and ^{1}H-NMR spectrophotometers.

Thin films of ABPEs were obtained by dissolving the ABPEs in N,N-dimethylformamide (DMF) and spin-coating onto glass slides and dried in a vacuum at 100℃ for 12h. The structures of ABPEs were confirmed using FT-IR spectroscopy and ^{1}H-NMR spectroscopy. The thermal properties of ABPEs were measured by means of differential scanning calorimetry (DSC). The optical properties of ABPEs were measured by UV spectrophotometer and Fluorescence emission spectrophotometer.

RESULTS AND DISCUSSION

We synthesized two polyethers (ABPE6 and ABPE12) by the polycondensation reaction in the presence of a phase transfer catalyst. The structures of ABPEs were characterized by FT-IR spectra and ^{1}H-NMR spectra. ABPE6 and ABPE12 had the average molecular weight (M_w) of 49,000 and 67,000, respectively. From DSC, the glass transition temperature (T_g) of ABPE6 and ABPE12 was found to be 112℃ and 110℃, respectively. The relatively high T_g of the ABPEs is attributed to the structure of main-chain polyethers containing conjugated aromatic ring and azo group in the backbone, giving considerable stiffness to the polymer. The length of the flexible spacer has less influence on the thermal stability of the ABPE*n*.

The optical properties of ABPEs were measured by UV spectrophotometer and Fluorescence emission spectrophotometer. In Figure 2, UV absorption spectrum of ABPE6 film at 25℃ showed two absorption peaks with maxima at 370 nm and at 470 nm in the 350-500 nm spectral region. Fluorescence emission spectrum of ABPE6 showed a peak with maximum at 669 nm. In Figure 3, UV absorption spectrum of ABPE12 showed two absorption peaks with maxima at 320 nm and at 400 nm in the 300-500 nm spectral region. Fluorescence emission spectrum of ABPE12 with the excitation of 400nm showed a peak with maximum at 656 nm. As the length of the flexible spacer increase, the absorption maximum shifts to longer wavelengths (from 370 nm to 400 nm) and the emission intensity significantly increases, as shown in Figure 2 and 3.

The red shift and the enhanced fluorescent emission may suggest that more intramolecular charge transfer complex in the lowest excited state are formed from the nitrogen lone pair in azo group to π^* antibonding acceptor in conjugated aromatic ring, when the length of the flexible space is longer. Futher experiments to synthesize ABPEn with more various n are now undertaking to explain the cause of the red shift and the enhanced fluorescent emission in a systematic way.

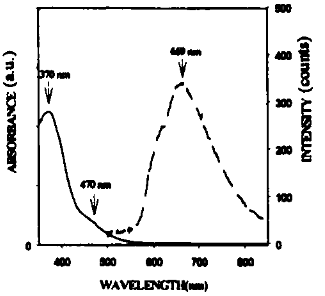


FIGURE 2 UV absorption (solid line) and fluorescence emission (short dashed line) spectra of ABPE6.

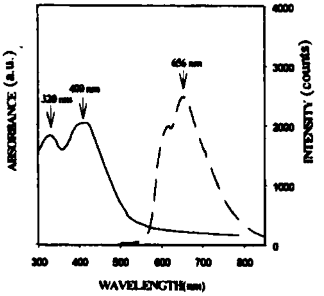


FIGURE 3 UV absorption (solid line) and fluorescence emission (short dashed line ; λ_{ex} = 400nm) spectra of ABPE12.

Acknowledgments

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