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Synthesis and Characterization of Hyperbranched Polymer for Second-Order Nonlinear Optics

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Abstract A new hyperbranched polymer was prepared by the one-pot Knoevenagel polycondensation of 4-[*N*,*N*-bis(hydroxyethyl)amino-4'-formyl]-azobenzene (CHO-DOH) with cyanoacetic acid using 4-(dimethylamino)pyridine (DMAP) as a base in tetrahydrofuran (THF). This polymer was soluble in polar aprotic solvents such as *N*,*N*-dimethylformamide and dimethyl sulfoxide. The glass transition temperature (T_g) of the polymer was observed at 145°C for PE-Azo/Hyper. The second harmonic generation (SHG) measurements of the obtained polymer were carried out by the Maker fringe method after corona poling at 7 kV near T_g for 10 minutes. The second-order nonlinear optical coefficient, d_{33} was about 15 pm/V for PE-Azo/Hyper.

INTRODUCTION

As nonlinear optical (NLO) materials, polymers have been considered the most promising candidates for making optical devices because of their fast response time, low absorption loss, environmental resistance, good mechanical strength and the possession of variable molecular designs as compared with inorganic materials [1].

During the past 5-10 years, research on NLO polymers has been focused on one-dimensional NLO polymers. In recent years, however, NLO polymers with unusual architectures have been prepared. These were sheet-like two-dimensional polymers as well as three-dimensional structures such as dendrimers and hyperbranched polymers. Among them, the hyperbranched polymers derived from AB_2 monomers

(described by Flory in 1952) are highly branched non-crosslinked polymers [2,3]. Although these polymers have high degree of branching like dendrimers, they do not have symmetrical structure.

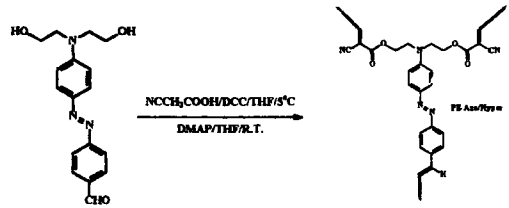
In this paper, we report the synthesis and characterization of a new hyperbranched polymer from an AB_2 type monomer, CHO-DOH.

EXPERIMENTAL

Synthesis of polymer PE-Azo/Hyper

To 0.50 g (2.39 mmol) of CHO-DOH and 0.43 g (5.00 mmol) of cyanoacetic acid in 10 mL anhydrous THF at 5℃ for 2 h. The solution was then filtered from dicyclohexylurea. To this solution at room temperature was added 0.40 g (3.28 mmol) of DMAP. THF was removed by a nitrogen purge. The polymer was dissolved in DMF and purified by reprecipitation into methanol. Yield: 0.65 g (95.59%). (Scheme 1). FT-IR (KBr pellet, cm^{-1}): 3400-3300 (Ar-CH), 3000-2800 (CH), 2220 (C ≡ N), 1750 (C=O), 1600 (C=C), 1350-1000 (C-N), 1300-1000 (C-O), ^{1}H-NMR (DMSO-d_6): δ = 3.6 (4H, N(CH_2CH_2-)$_2$), 3.9 (4H, N(CH_2CH_2-)$_2$), 6.7 (2H, Ar C*H*), 7 (2H, Ar C*H*), 7.5, 7.6 (4H, Ar C*H*), 7.8 (H, -C*H*=C)

SCHEME 1. Synthetic route of PE-Azo/Hyper



Film preparation and poling

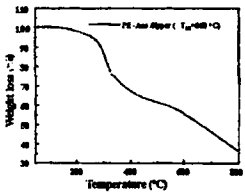
Polymer films of PE-Azo/Hyper were prepared by spin coating from 7 wt.% polymer solutions dissolved in cyclohexanone/DMF (1:1). The solution was first filtered through a 0.45 μm syringe filter to move insoluble particles, then spun onto an clear indium tin oxide (ITO) glass

plate at 900-1,000 rpm for 50 sec. It was finally dried in a vacuum oven at 30°C for 24 h. The corona poling technique was performed using the positive polarity of a 25 μm thick tungsten wire. The tungsten wire was positioned normal to the film surface with a wire-to-film distance of 1.5 cm. The PE-Azo/Hyper films were poled under 7 kV at near 145°C for PE-Azo/Hyper for 10 minutes and then cooled down to ambient temperature while under continuous poling.

RESULT AND DISCUSSION

Hyperbranched polymer can easily be synthesized and shows good solubility so as to make possible to produce good quality film. The thermal behavior of this polymer was studied by DSC. It was found that the T_g of this polymer was about 145°C. As determined by TGA, Fig. 1 shows initial decomposition temperature (T_{id}) of PE-Azo/Hyper. T_{id} at 240°C is due to the thermal breaking of azo group. The polymer could be dissolved in polar aprotic solvents such as *N,N*-dimethyformamide (DMF), dimethyl sulfoxide (DMSO), and *N*-methyl-2-pyrrolidone (NMP). The weight average molecular weight (M_w) was determined to be 61,800 (M_w/M_n=1.86) by the gel permeation chromatography using polystyrene as the standard. The intrinsic viscosity of PE-Azo/Hyper obtained from DMF solution at 25°C was 0.31 dL/g. UV/visible absorption spectra of polymers and monomers are shown in Fig. 2. The absorption maxima of the NLO chromophore in CHO-COH and PE-azo/Hyper were at 475 and 438 nm, respectively. In polymer data the absorption spectra of before and after poling are shown. After the molecular dipoles were aligned along the direction of the high electric field, the shift in the maximum as well as the reduction in the absorption intensity were observed. To characterize the poling efficiency the order parameter $\Phi = 1 - A_1/A_0$ (A_1 is the absorption intensity of the poled film and A_0 is the absorption intensity of unpoled film) was used. The order parameter of PE-Azo/Hyper was 0.17. For

evaluating the NLO activity, Maker fringe method with a Nd:YAG laser operating at 1064 nm was used. Maker fringe patterns of angular SHG dependence for the polymer film was recorded and then compared with the values obtained form a Y-cut quartz plate as a reference (d_{11} = 0.5 pm/V). The second-order nonlinear coefficients (d_{33}) of PE-Azo/Hyper was about 15 pm/V (Fig. 3).



FIGRUE 1. TGA thermogram of PE-Azo/Hyper

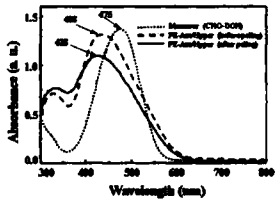


FIGURE 2. UV/vis spectra of CHO-DOH and PE-Azo/Hyoper

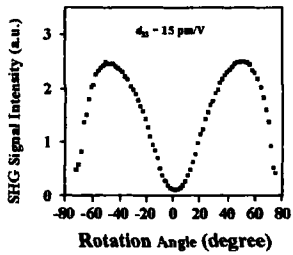


FIGURE 3. SHG signal intensity of PE-Azo/Hyper

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