A Hyperbranched Nonlinear Optical Polyester with Polar Chromophores

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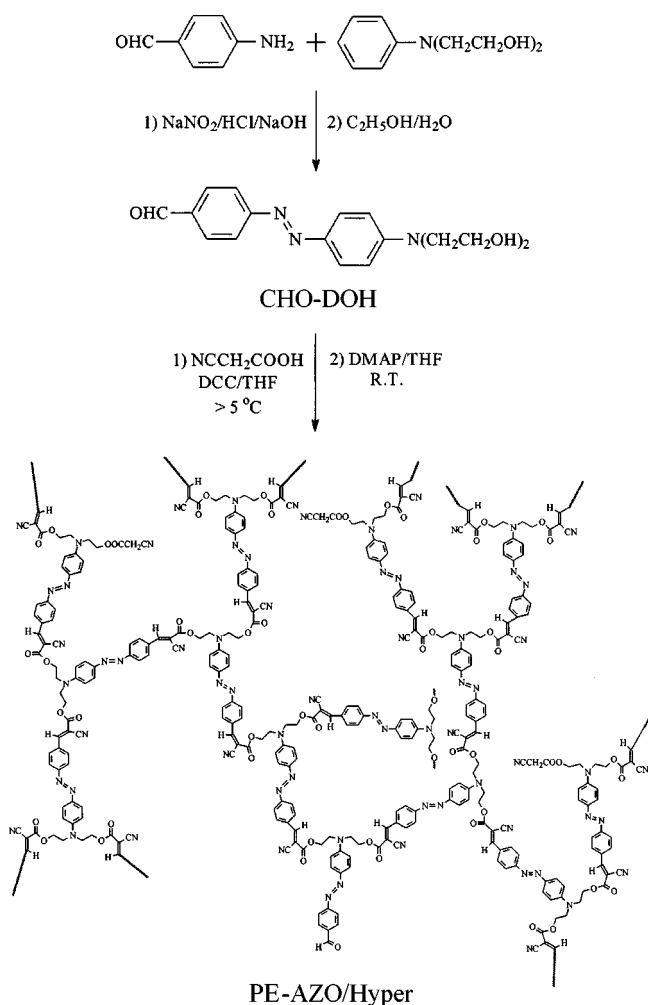*Received May 10, 2000*

Second-order nonlinear optical (NLO) polymeric materials have been recognized as the promising candidates for various photonic devices such as electro-optic modulators, optical switches and frequency doublers.[1-5] These interests in polymers arise from their large NLO activities, low dielectric constants, excellent processability, high optical damage threshold, etc. Several strategies for making NLO polymer systems have been proposed. Those are side-chain polymers and main-chain polymers of one-dimensional types in which NLO active chromophores are incorporated either by attaching to an amorphous polymer, or into a polymer backbone.[6-11] In addition, a 3-dimensional polymeric network structure

CHO-DOH

PE-AZO/Hyper

Scheme 1

with NLO chromophores can be obtained through thermally or photochemically induced crosslinking reactions.[12,13] However, the crosslinked systems have the problem of large optical losses by limited uniformity of the crosslinking reaction. In order to get new 3-dimensional NLO polymeric systems without crosslinked structure, we have developed a hyperbranched polymer which has highly branched non-crosslinked structure derived from AB_n ($n > 1$) type monomer proposed in the literature.[14,15]

The synthetic pathway of the monomer and hyperbranched polymer is presented in Scheme 1. The monomer, 4-[*N,N*-bis(hydroxyethyl)]amino-4'-formylazobenzene (CHO-DOH) can be prepared by the diazotization of *p*-aminobenzaldehyde and *N*-phenyldiethanolamine in aq. HCl. A NLO hyperbranched polymer (PE-Azo/Hyper) was obtained with a 95.6% yield from CHO-DOH and cyanoacetic acid in a single-step reaction by the Knoevenagel polycondensation using 4-(dimethylamino)pyridine as a base. The monomer and polymer were characterized by IR and NMR spectroscopies. Their results are in good agreement with the structure obtained in the synthetic route.[16]

The resulting hyperbranched polyester was soluble in polar aprotic solvents such as *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), etc. and could be processed into high optical quality films by spin coating. The weight average molecular weight ($\overline{M}_w$) was determined to be 61,800 ($\overline{M}_w/\overline{M}_n$=1.86) by the gel permeation chromatography using polystyrene as the standard. No melting transition detected on differential scanning calorimetry (DSC) indicates that this polymer is amorphous. It showed a glass transition temperature of 121 °C. Thermal stability of the PE-Azo/Hyper was studied by using thermal gravimetric analysis (TGA) and the initial decomposition occurred at 240 °C in air. This degradation process was confirmed as the decomposition (N_2 fragments generation) of the azo group in chromophore according to the TGA-Mass spectroscopy analysis.

The UV-vis absorption spectra of the monomer and the polymer are shown in Figure 1. The absorption maxima for the π-π* transition of the NLO chromophore in CHO-DOH and PE-Azo/Hyper were at 475 and 438 nm, respectively. This means that the introduction of the NLO chromophore into the hyperbranched polymer chain causes a 37 nm blue shift in its intrinsic absorption. This phenomena may be due to an electronic interaction between chromophore units and polymer chains.[7] Polar alignments of NLO chromophores in hyperbranched polymer films were achieved by a corona poling method using a tungsten wire as an electrode placed 1.5 cm above the film surface. Strong electric potential of 7
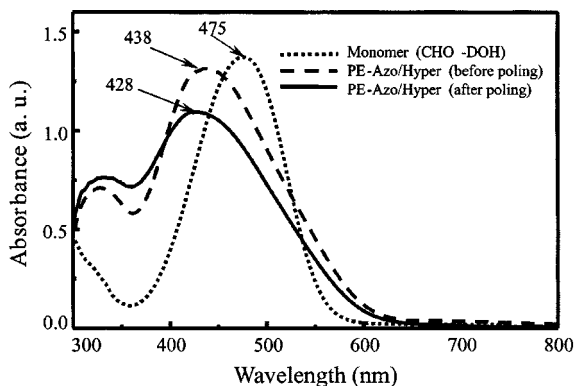
Figure 1. UV-vis absorption spectra of monomer CHO-DOH and polymer PE-Azo/Hyper films on glass substrates before and after poling.
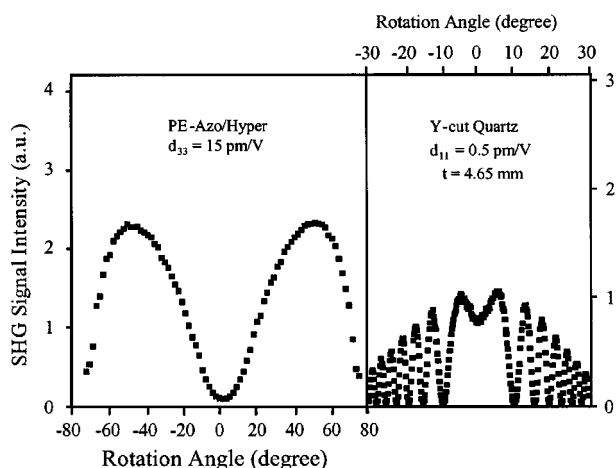

Figure 2. Angular dependence of SHG signals in a poled PE-Azo/Hyper film and that of Y-cut quartz plate.

kV d.c. voltage was applied between the anode and the ITO electrode. The absorption intensity of this poled film was reduced due to the polar alignment of chromophore dipoles. The reason for a 10 nm blue shift (from 438 to 428 nm) of the maximum absorption peak for the poled film is probably due to the electronic environmental change between chromophores and polymer backbones by the polar alignment. The order parameter was determined from absorption spectra using the equation of $\psi = [3(\cos^2\theta)-1]/2 = 1-A_T/A_P$ (where θ is the angle between the dipole moment of the chromophore and the normal to the film surface. A_T and A_P are the absorption intensities before and after poling). From this equation we obtained the order parameter of $\psi = 0.17$. It was found that this value was sustained without any decreases at room temperature for 90 days, hence showing an excellent temporal stability of chromophore alignment in our hyperbranched polymer.

The second harmonic generation (SHG) measurement was performed on the poled film using Q-switched Nd:YAG laser with the wavelength of 1064 nm. Maker fringe patterns of angular SHG dependence for the polymer film was

recorded and then compared with the values obtained from a Y-cut quartz plate as a reference ($d_{11} = 0.5$ pm/V).[17] From the calculation, we obtained a sizable d_{33} of 15 pm/V from hyperbranched polymer, but its value was not high as we expected. This result can be probably caused by the limited dipolar alignment of chromophores at the cross positions or entangled sites of the branches in the polymer. Detailed studies on the linear and nonlinear optical properties as well as thermal and temporal stabilities of this hyperbranched polymer are now in the progress.

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16. CHO-DOH: FT-IR (KBr pellet, cm^{-1}) 3500-3200 (OH), 3000 (Ar-CH), 2850-2750 (Al-CH), 1725 (C=O), 1600 (C=C), 1350-1300 (C-N), 1250-1000 (C-O); ^{1}H NMR (CDCl$_3$, 300 MHz, ppm) δ 3.6-3.8 (8H, N(CH_2CH_2OH)$_2$), 4.2 (2H, OH), 6.8-8.1 (8H, Ar-CH), 10.25 (1H, CHO). PE-Azo/Hyper: FT-IR (KBr pellet, cm^{-1}): 3400-3300 (Ar-CH), 3000-2800 (Al-CH), 2220 (C≡N), 1750 (C=O), 1600 (C=C), 1350-1000 (C-N), 1300-1000 (C-O). ^{1}H NMR (DMSO-d_6, 300 MHz, ppm): δ 3.6 (4H, N(CH_2CH$_2$-)$_2$), 3.9 (4H, N(CH$_2$CH_2-)$_2$), 6.7-7.6 (8H, Ar-CH), 7.8 (1H, -CH=C).
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