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Poling Behavior of Electro-Optic Polymers with Perfluorinated Chromophores

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A benzoxazole-based NLO chromophore with perfluorobutyl side chain was newly synthesized. The poling behavior of an NLO polyester therefrom was investigated by a second harmonic generation and a simple reflection measurement. The electro-optic coefficients of the polyester was measured in the range of 8~10 pm/V at 1.3 μm.

Keywords: electro-optic polymer; perfluorinated benzoxazole chromophores

INTRODUCTION

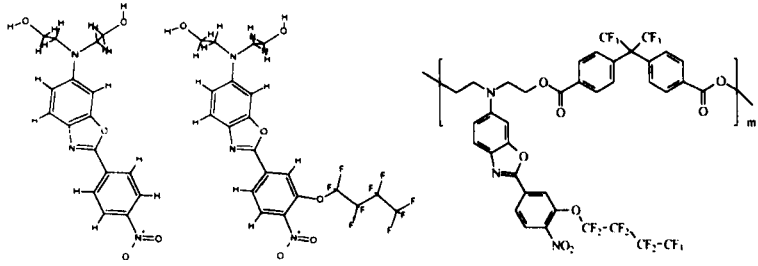
As a strategy for enhancing second-order nonlinear optical (NLO) activities, we need to develop an NLO chromophore with large hyperpolarizability (β) and dipole moment (μ_0), to maximize the number density (N) of chromophores in polymers, and to increase the efficiency of chromophore alignment (θ).[1] In order to align effectively the chromophores, we propose a unique NLO chromophore with perfluorinated tail structure. We expected that the bulky and flexible tail structure offers more free volume between chromophores and polymers to be able to give larger order parameters at electric poling. On the other hand, the main reason of the high optical loss of

electro-optic polymeric systems in the infra-red region is mainly due to their high C-H bond vibrational absorption in the telecommunication wavelength of 1.3 μm and 1.55 μm.[2] From these reasons, our new NLO benzoxazole chromophores with perfluorobutylated tail is believed to be an advanced material for low optical loss as well as high NLO activity. In this study, the poling and relaxation behavior of NLO polyesters with perfluorinated chromophore was investigated by an electro-optic measurement.

RESULTS AND DISCUSSION

Synthesis of NLO Monomer and Polymer

A diol monomer (9FBz) was synthesized by a reaction of 2-amino-5[di(2-hydroxyethyl)amino]phenol and 4-nitro-3-(1,1,2,2,3,3,4,4,4-nonafluoro butoxy)benzaldehyde, and a subsequent oxidation.[3] The calculated molar volume and polarizability of 9FBz were larger than those of Bz due to the bulky and polar perfluorobutylated tail structure in chromophore (TABLE I).



Bz 9FBz 15FPST

FIGURE 1. The structures of NLO monomers and polyester.

The NLO polyester (15FPST in FIGURE 1) was synthesized by polycondensation of a 9FBz with 4,4'-(hexafluoroisopropylidene)bisbenzoyl chloride. The calculated and measured fluoride content of the polyester was 30.53 and 31.0 %, respectively.

TABLE I. Calculated properties of NLO monomers

	Bz	9FBz
Formula(M.W.)	$C_{17}H_{17}N_3O_5$(343.336)	$C_{21}H_{16}F_9N_3O_6$(577.357)
Molar Volume (cm^3)	242.7±3.0	365.4 ±3.0
Index of refraction	1.685 ±0.02	1.537 ±0.02
Polarizability ($10^{-24}cm^3$)	36.57 ±0.5	45.26 ±0.5

Electro-optic properties

The 15FPST was dissolved in 1,1,2,2-tetrachloroethane/DMF(1/1) at 15 wt % concentration. Thin films with a thickness of 1~3 μm could be spin-casted onto ITO glasses depending on spin speed. All films were dried at 170 ℃ for 2 h to remove solvent prior to poling, and then gold electrode was evaporated onto the films. The films for measurement of electro-optic coefficient (r_{33}) were conducted by electric poling at various conditions. The r_{33} was measured by the well known simple reflection method at a wavelength of 1.3 μm. To investigate a proper poling temperature of 15FPST, second harmonic (SH) intensities during *in-situ* corona poling were measured according to increasing temperature. As shown in FIGURE 2, the SH intensities increased steeply above 170 ℃, where is ascribed to the glass transition temperature.

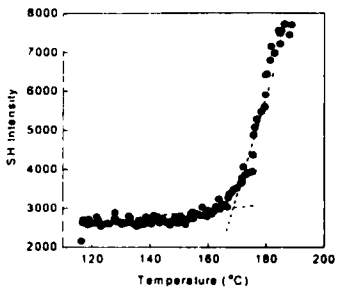


FIGURE 2. The SH intensities vs. temp.

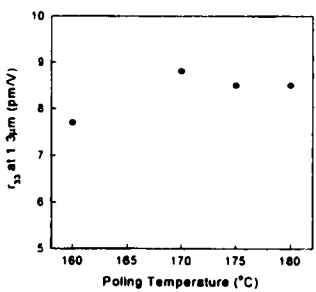


FIGURE 3. r_{33} vs. poling temp.

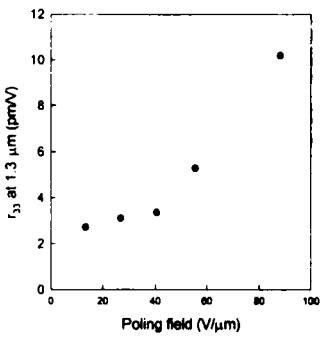


FIGURE 4. r_{33} vs. poling field.

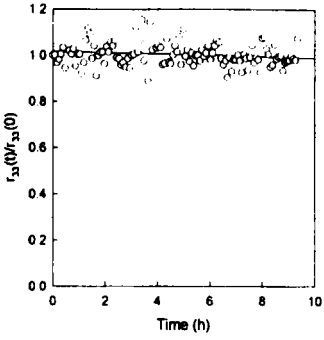


FIGURE 5. Temporal stability of r_{33} of 15FPST at 100 ℃.

FIGURE 3 shows the r_{33} depending on poling temperatures. The r_{33} value poled at 170 ℃ was measured to 8.9 pm/V and the r_{33} value poled at below and above the temperatures were smaller. FIGURE 4 is the dependence of r_{33} on poling field, showing that the r_{33} increased linearly according to poling field. The r_{33} at a poling field of 0.9 V/μm was 10.1 pm/V. The r_{33} value retained >95 % of original value at 100 ℃ after 10 h as shown in FIGURE 5, which indicates the excellent temporal stability of r_{33}.

In summary, the fluorinated NLO polyester is found to be a promising candidate for practical electro-optic devices materials.

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