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Ju Sik Kang [a] , Hyeon Taik Hong [a] & Dong Hoon Choi [a]

[a] Division of Textile, Chemical, and Industrial Engineering, Institute of Material Science & Technology, I.L.R.I, Kyung Hee University, Kyungki, 449-701, Korea

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JU SIK KANG, HYEON TAIK HONG and DONG HOON CHOI

Division of Textile, Chemical, and Industrial Engineering, Institute of Material Science & Technology, I.L.R.I, Kyung Hee University, Kyungki 449–701 Korea

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We synthesized the second-order nonlinear optical (NLO) copolymers for studying the effect of temperature on the temporal stability of electro-optic effect. Heterocyclic azo chromophore was synthesized to be bound to methacrylate and naphthalate polymer backbone. Particularly, amino methylsulfonylbenzothiazole was employed to prepare the azo chromophore. Second harmonic generation can give us the relationship between the second harmonic signal and sample temperature during corona poling. The decaying behavior of second harmonic signal was traced at different temperature that is in the vicinity of the glass transition temperature.

Keywords: heterocyclic chromophore; second harmonic generation

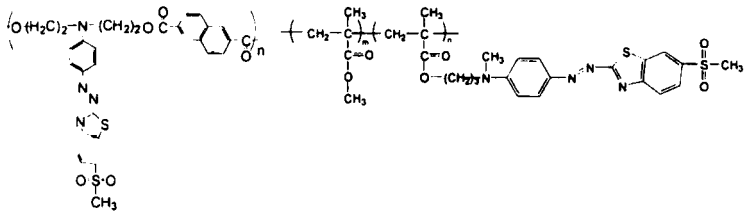
INTRODUCTION

Nonlinear optics (NLO) is an important field of photonics whose technology includes acquisition, storage, process, and transmission of photons instead of electrons in signal processing. Organic nonlinear optical (NLO) materials provide strong potential advantages for second harmonic generation and electro-optic applications.[1-3] Particularly, poled polymeric systems have drawn remarkable interests in recent years as promising candidates for application in electro-optic and photonic devices. In an attempt to investigate the rate of molecular relaxation in the chromophore after poling, we

designed two polymers. One is composed of relatively long repeating unit with short side chain group. The other consists of relatively short repeating group with long side chain group. Using two copolymers, we did *in-situ* second harmonic (SH) generation and traced the relaxation behavior of SH signal at the temperature higher than the glass transition temperature.

EXPERIMENTAL

The synthesis of two polymers will be described elsewhere. The structures of polymers were illustrated in Figure 1. The film was spun on normal borosilicate glass.



(a) (b)

FIGURE 1 Structures of polymers used in this study; (a) polynaphthalate; (b) polymethacrylate.

Second Harmonic Generation (SHG)

In-situ second harmonic generation (SHG) measurements of samples were carried out with a Q-switched mode locked, Nd^{+3}:YAG laser operating in the TEM_{00} mode. The samples were mounted on the hot stage and corona poled. The sample temperature was precisely controlled calibrating between the temperature of the heater and the sample. We integrated the second harmonic (SH) signal during corona poling for obtaining the temperature dependence of SH signal of each polymer film.

RESULTS AND DISCUSSION

The present work describes the second-order nonlinear optical properties of active polymers with simple structure and chromophore for attaining the high NLO activity and investigating the relaxation of molecular alignment after poling. Polynaphthalate was prepared with naphthalene dicarboxylic acid (NDA) and chromophoric diol compound *via* Mitsunobu reaction. The glass transition temperatures of two polymers were obtained from DSC thermograms. The glass transition temperatures of polynaphthalate and polymethacrylate were found to be 152°C and 145°C respectively.

We integrated the SH signal with the increase of the sample temperature under 6KV, corona field. The signal slowly increased even at the temperature slightly lower than T_g. In both samples, the signal was abruptly increased around 140-155°C which is well consistent with the range of T_g (Figure 2). It is quite reasonable that the large segmental motion of the main chan can accelerate to form a noncentrosymmetric structure of the chromophoric groups. In order to compare the temporal stability of two polymers, we traced decaying SH signal without corona field at certain temperatures. Two temperatures (T_1, T_2) were set, which are T_1/T_g=1 and T_2/T_g =1.01. In the case of polymethacrylate, the relaxation is much slower than that of polynaphthalate at T_g and the temperature higher than T_g (Figure 3). The chromophore was bound to relatively long repeating unit without any spacer in polynaphthalate. Therefore, as the temperature was raised higher than T_g, larger free volume around the main chain can accelerate the motion of the side chain group. The chromophore is less geometrically hindered so that the molecules are more labile to move. Even though the glass transition temperature is very high, the stability can be poor at the temperature higher than T_g. The temporal stability of NLO effect in poled polymer is strongly dependent on the geometrical structure of side chain and main chain over a wide range of the temperature.

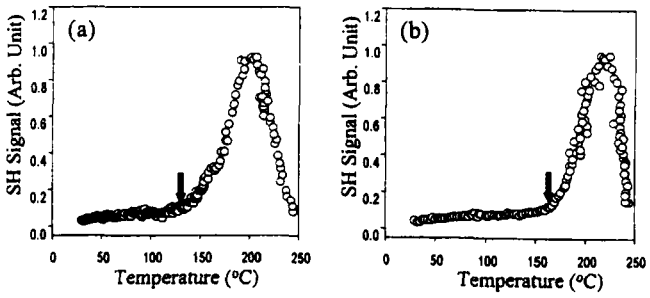


FIGURE 2 Temperature dependence of SH signal: (a) polymethacrylate; (b) polynaphthalate; corona voltage 6 kV.

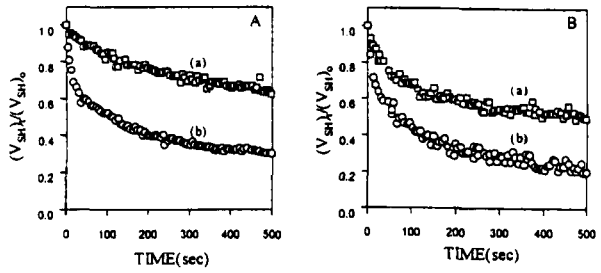


FIGURE 3 Decaying behavior of SH signal: A, at T_1/T_g=1; B, at T_2/T_g=1.01: (a) polynaphthalate; (b) polymethacrylate.

Acknowledgment

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