

Nonlinear Optical Polymers Possessing Thermal and Temporal Stability: Potentials and Prospect

Dong Wook Kim¹, Hyun Kyung Ju¹, Soo Mi Ahn¹, Sung Cheol Yoon¹,
Jong Sun Lim¹, Seung Ku Park², Changjin Lee¹

¹Advanced Materials Division, Korea Research Institute of Chemical
Technology, Daejeon, Korea

²Electronics and Telecommunication Research Institute, Daejeon,
Korea
cjlee@kriict.re.kr

Introduction

Optical modulator is an essential device in the telecommunication network in order to translate electrical information into an optical signal. Although the inorganic substance, lithium niobate is currently serving as a core material for the device, the high production cost and intrinsic large phase mismatch between infrared and millimeter wave frequencies pressed scientists to find alternatives. Many scientists have recognized the nonlinear optical (NLO) organic polymers as a promising candidate for such a role due to their intrinsically low dielectric constant, simple procedure for the devices, easy structure tailoring for certain purposes, and large macroscopic optical nonlinearity. After a couple decades of research, a significant progress has been achieved in the NLO polymers which are near the commercialization. Still few critical hurdles remained to be solved. One of the critical issues is to prepare an NLO polymer which produces a high quality optical coating and good thermal durability. It is extremely difficult to prepare an NLO polymer which satisfies both properties at the same time. Thus, the molecular design should be compromised.

Polyimides have played a key role in the materials for the microelectronics, appliances, and other specialties largely due to their superior thermal stability, chemical resistance, and mechanical durability. Such performance has lured many researchers to utilize the materials for the electro-optic applications, too. In this work, we prepared thermally durable polyimides appended with NLO chromophores, which were designed to have good thermal and photochemical stability as well as high electro-optic activity. NLO chromophores were synthesized and characterized well by NMR, mass spectroscopy, absorption spectroscopy, DSC, and TGA. The chromophores were covalently bonded with the polyimide backbone via Mitsunobu coupling in a good yield. The resulting NLO polymers were characterized by ¹H-NMR, GPC, DSC, and TGA. Macroscopic optical nonlinearity was also evaluated by measuring their electro-optic coefficient by simple reflection method using 1550 nm laser light.

Experimental

Synthesis of hydroxyl polyimide. BAHF (7.325 g, 0.02 mol) was dissolved in anhydrous DMAc (60 mL) solution under nitrogen purging at room temperature. ODPAA (6.204 g, 0.02 mol) and PA (0.296 g, 0.002 mol) were quickly added into the solution under nitrogen purging. The solution was vigorously stirred with a mechanical stirrer for 24 h. Pyridine (3.16 g, 0.04 mol) and acetic anhydride (4.08 g, 0.04 mol) were added to the reaction solution. The solution was vigorously stirred with a mechanical stirrer for additional 6 h. The solution was then slowly dropped into methanol/water (9/1) mixture to precipitate a white or light yellowish solid. The solid was filtered and then placed in a vacuum oven. The solid was dissolved in THF (100 mL) and then added into methanol/water (9/1) mixture to reprecipitate a solid. The solid was annealed at 210 °C for 6 h in the vacuum oven to produce a fully cured polyimide. The solid was dissolved in THF (100 mL) and then added into methanol/water (7/3) mixture to reprecipitate a solid, in order to remove out any impurities or unreactants. The solid dried at 80 °C under vacuum for 24 h.

¹H-NMR (DMSO, ppm) δ 10.42 (s, 2H), 7.95-7.92 (d, J = 8.9 Hz, 2H), 7.53 (m, 4H), 7.34 (s, 2H), 7.16-7.13 (d, J = 8.3 Hz, 2H), 7.02-7.00 (d, J = 8.6 Hz, 2H).

Coupling of NLO chromophores with hydroxyl polyimide.

NLO chromophores with a terminal hydroxyl group have been synthesized by coupling between aminobenzene or julolidine donor and phenylene bridge, and then subsequent coupling between the resulting product and tricyanofuran acceptor. The chromophores

were chemically bonded to the polyimides backbone through Mitsunobu reaction as follows. Diethyl azodicarboxylate (DEAD) (0.82 g, 4.69 mmol) was added dropwise for 4-6 hrs into a solution of hydroxyl polyimide, triphenylphosphine (1.23 g, 4.69 mmol), and NLO chromophore in THF (50 mL) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 48 h. The resulting reaction mixture was precipitated into methanol with a vigorous stirring. The collected precipitate was dissolved in THF (100 mL) and reprecipitated into the solution of methanol in a high-speed blender. The precipitate was filtered and washed with methanol. The solid dried at 80 °C under vacuum for 2 h to produce dark blue solid (PI-StTCF).

Results and discussion

Chemical structure of the NLO chromophores was verified by ¹H and ¹H-¹H COSY NMR spectroscopy. The coupling constant as large as 15 Hz in the NMR spectrum indicated that the double bonds linking the donor, the conjugation bridge, and the acceptor have a trans-conformation. The absorption spectra were obtained in chloroform and toluene to determine the absorption maximum for the charge transfer band. DSC and TGA data showed that melting points of the chromophores were ranged from 170 to 200 °C with a sharp endothermic peak and all the chromophores were thermally stable up to 220 °C in nitrogen atmosphere.

Soluble hydroxyl polyimides were prepared by a direct polycondensation of diaminophenol and aromatic dianhydride. GPC analysis showed that the hydroxyl polyimide had the average molecular weight of about 15,000. The polyimide thermally endures up to 350 °C as traced by TGA analysis. DSC data showed that the hydroxyl polyimide exhibited as high T_g as 275 °C. The chromophores were coupled into the polyimides through Mitsunobu reaction. The resulting NLO polyimide was characterized to show around 170 °C of T_g by DSC measurement (Figure 1) and the initial weight loss started at 190 °C.

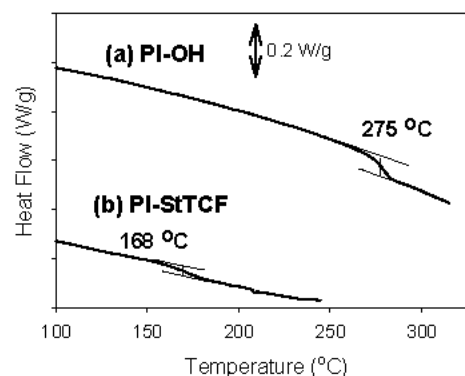


Figure 1. DSC thermograms of (a) hydroxyl polyimide (PI-OH) and (b) NLO polyimide (PI-StTCF).

We obtained optical quality films by spincoating of the solution of the NLO polyimide and evaluated their electro-optical properties by a simple reflection method at 1550 nm. Optimum poling temperature was found to be around 175 °C, which was slightly higher than T_g of the polymer. The electro-optic coefficient was measured to be about 30 pm/V. Temporal stability was also evaluated at high temperature. More than 90 % of the initial electro-optic coefficient value was maintained over 300 h at 85 °C.

Acknowledgement. This work was financially supported by the Ministry of Commerce, Industry and Energy for NT-IT Fusion Strategy of Advanced Technology.

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