Synthesis of Nonlinear Optical Polymers with Enhanced Thermal Stability

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Abstract

In order to enhance the thermal stability, three kinds of benzoxazole-based NLO polymers were prepared: polyimide and polyester with pendant benzoxazole unit, and main-chain polybenzoxazole. The resultant polymers had a high glass transition temperature in the range of 170 - 195℃ and initial decomposition temperatures were over *ca.* 250 ℃. The electro-optic coefficient (r_{33}) of poled polymer films were measured by simple reflection method, and their NLO activity was quite stable during long period.

Introduction

For development of photonic devices, such as electro-optic (EO) modulator, optical switch and optical memory, polymeric nonlinear optical materials offer several advantages over crystals, such as larger second-order hyperpolarizability (β), excellent processability, low costs, and great flexibility in design and optimization of materials.[1] However, during the prolonged periods, optical nonlinearity of polymeric material tends to decay gradually, which is considered as drawback for polymeric system to overcome. In our previous study, it was found that benzoxazole chromophores exhibit the excellent thermal stability, much better than conventional stilbene- or azo-based dyes.[2]

In this work, in an attempt to prepare NLO polymers with high stability, three benzoxazole-based polymers were synthesized and their physical properties were characterized.

Experimental

Synthesis of NLO polymers

The synthetic schemes for NLO polymers are shown in Figure 1.

Polyimide with pendant benzoxazole unit (**12FPIBz**): Fluorinated polyimide (**12FPI**) was prepared by two-step condensation reaction. That is, **6FDAP** was reacted with **6FDA** via ring-opening polyaddition, followed by thermal cyclohydration. Then benzoxazole chromophors, prepared as described in elsewhere[3], were incorporated onto polyimide(**12FPI**) via Mitsunobu reaction[4] and finally **12FPIBz** was obtained. The chemical structures were characterized by H-NMR (Varian Gemini 200, 200 *MHz*) and FT-IR (Mattson Alpha Centauri) spectrometers.

Polyester with pendant benzoxazole unit (**15FPEBz**) was obtained by the reaction of dihydroxy benzoxazole chromophore reacted with fluorinated diacid chloride.[5]

Polybenzoxazole (**6FPBO-TCN**): Polybenzoxazole (**6FPBO**) was obtained by reacting diacid monomer containing *N*-phenyl group with 2,2-*bis*(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3,-hexafluroropropane in phosphorus pentaoxide/ methanesulfonic acid solution. The post-tricyanovinylation was carried out by reacting polymer (**6FPBO**) with tetracyanoethylene in DMF at 70 - 80°C.[6]

Sample preparation

Polymers, dissolved in 1,1,2,2,-tetrachloroethane (10 wt %), were spin coated onto ITO glass and thin films of ca. 1μm thickness were obtained. Then gold was evaporated at a top of film as electrode. For alignments of NLO chromophores, contact electrode poling was performed at near T_g and cooled with the electric field on.

Characterization

Absorption maxima (λ_{max}) of NLO polymers were determined with UV-VIS spectrometer (Shimatzu UV-240). Thermal transition behaviour of polymers were determined by Dupont Thermal Analyzer. The linear electro-optic coefficients of the poled samples were determined using a reflection method, proposed by Teng *et al.*[7]

Results and Discussion

Physical properties of NLO polymers are summarized in Table 1. Due to the high content of fluorine in backbone,[8] polymers exhibits good solubility in common organic solvents, in addition to high optical clarity and processability. The glass transition temperatures (T_g) of polymers are in the range of 170-195°C. Polyester and polybenzoxazole shows the lower T_g than polyimide, due to flexible aliphatic units along backbone.

Nonlinear optical coefficient (r_{33}), determined by simple reflection method is given in Table 2. The temporal stability of NLO polymer was investigated by monitoring the decay of EO coefficients (r_{33}) of poled films as a function of time at 100°C. Polyimide (12FPIBz) and polyester (12FPEBz) retain >90% of NLO activity for 33 hours and 10 hours at 100°C, respectively. Polybenzoxazole (6FPBO) exhibits better thermal stability, being compared with polymers with pendant benzoxazole group. 6FPBO retained over 90% of initial value of electro-optic coefficient, even after being subjected to thermal aging for 1 week at 100°C. The orientational stability of benzoxazole-based polymers results from the fact that motion of NLO chromophore is restricted due to the incorporation onto rigid polymer chain. However, it seems that the attachment of the NLO chromophores along polymeric backbone is more efficient method than that as pendant group.

References

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Figure 1. Synthesis of NLO polymers

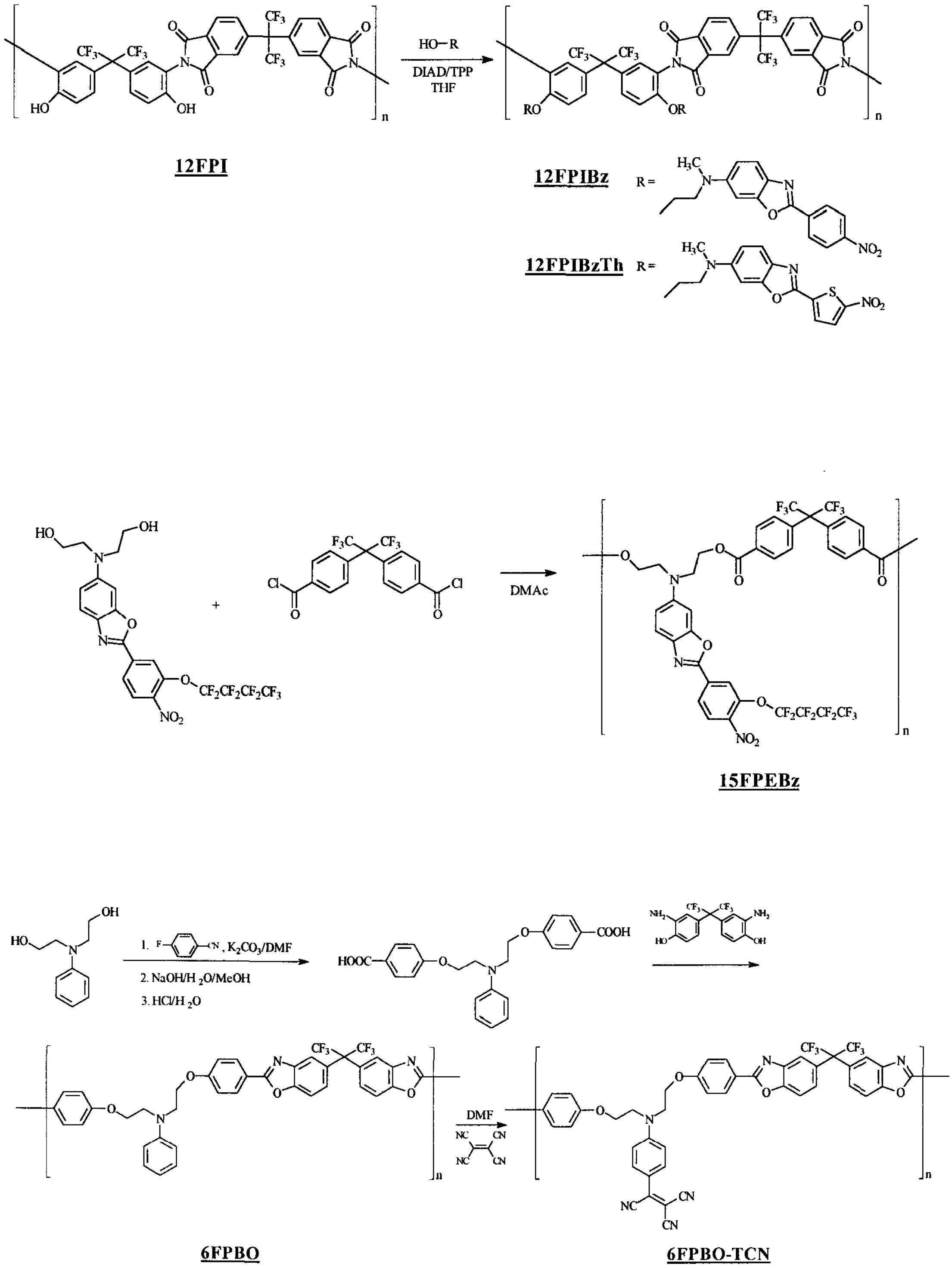

Table 1. Physical properties of NLO polymers

NLO Polymer		η_{inh} [a] (dL/g)	T_g [b] (℃)	T_d [c] (℃)	$\lambda_{max.}$ [d] (nm)	Solubility[e]		
						THF	Cy[f]	DMF
Polyimide	12FPIBz	0.33	195	250	427	◎	◎	◎
polyester	15FPEBz	·	170	300	430	◎	◎	◎
Polybenzoxazole	6FPBO-TCN	0.27	180		510	◎	◎	◎

[a]Determined at a concentration of 0.5 g/dL at 30 ℃ in NMP. [b]Glass transition temperatures measured by DSC at a heating rate of 20 ℃/min. [c]Initial decomposition temperature measured by TGA at a heating rate of 10 ℃/min under nitrogen. [d] Maximum absorption in film. [e]◎: Soluble. [f] Cyclohexanone.

Table 2. Nonlinear Optical properties of polymers

NLO Polymer		T_g [b] (℃)	r_{33} [a] (pm/V)	
			633 (nm)	1.3 (μm)
Polyimide	12FPIBz	195	·	8.5
Polybenzoxazole	6FPBO-TCN	180	34	·
polyester	15FPEBz	170	·	10.1

[a]Electro-optic coefficient (r_{33}) measured by simple reflection method.