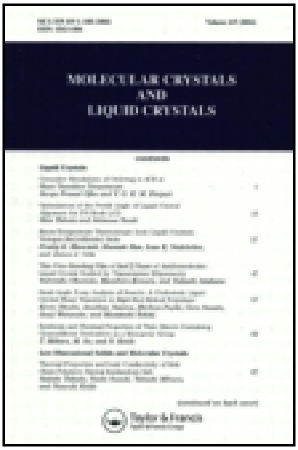

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Novel High Glass Transition Temperature Polyurethanes Functionalized with Efficient CT Chromophores for Second Order NLO Applications

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In this paper we describe the synthesis of a new class of high glass transition temperature polyurethanes functionalized with two quasi 1D charge transfer dyes. The polymers are soluble in several organic solvents and can be processed into thin films by spinning technique. The polymers were synthesized in view of their application in second order nonlinear optics for optical signal transmission. The active chromophores, exhibiting large first hyperpolarizabilities $\beta(-2\omega;\omega,\omega)$ were poled by the corona poling technique. The kinetics of poling and of relaxation were studied by second harmonic generation technique.

Keywords: corona poling; functionalized polyurethanes; NLO chromophores; second harmonic generation

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INTRODUCTION

One of the important issue in this centaury is the development of information society with an almost unlimited transfer of information. This requires broad transmission systems. One of the key element in these systems are electro-optic modulators (EOMs), allowing to transfer any signal to a travelling optical beam. Performant, large band EOMs require efficient second order nonlinear optical (NLO) materials with fast response. Organic molecules, and particularly the charge transfer (CT) quasi 1D structures emerged as potentially good candidates for EOM application. A lot of effort has been done in designing, synthesis of new NLO active CT chromophores and in understanding of the origin of large NLO response through the molecular engineering approach [1,2]. However in device applications important is the macroscopic NLO response, important for practical applications, which depends on the structure of bulk materials. The CT molecules with large first hyperpolarizabilites β exhibit also a large ground state dipole moment. The dipole–dipole interaction usually tends to align them antiparallel leading to a centrosymmetric material with no quadratic NLO response. Also most of applications are targeted in waveguiding configuration. Therefore it is very important that a given material is processable into good optical quality thin films. Consequently a lot of effort is done from the point of view of material processing into noncentrosymmetric thin films with large second order NLO susceptibility $\chi^{(2)}$. Several techniques were developed for organic noncentrosymmetric thin film fabrication such as: Z-type Langmuir-Blodgett films [3], self assembly [4], molecular epitaxy or pseudoepitaxy [5]. However the most promising appear to be poled polymers (for a review see e.g., [6,7]). These materials marry good processability and good optical propagation properties, which are due to the amorphous character of polymer matrix and its solubility with large second order NLO response obtained by functionalizing these polymers with active, efficient NLO chromophores and their orientation by a static (electrode or corona, see. e.g., Ref. [7]) or optical electric field [8]. However there are several important factors which have to be addressed, such as the stability of induced polar order, optimal density of chromophores, which depends on the aggregation leading to large propagation losses, chemical and photostability of chromophores and of the matrix. The stability of induced order depends very much on the difference between the orientation and the operation temperatures. Higher is the glass transition temperature less relaxation will occur. Therefore it is also important to synthesize polymers with as large as possible glass transition temperature.

In this article we describe the chemical synthesis of two new efficient NLO chromophores. The chromophores were grafted on polyurethanes, known to exhibit a high glass transition temperature. For the sake of comparison the same chromophores were also grafted on a polyester backbone. The polymers are soluble and can be processed into thin films by spinning technique. The refractive indices of spun films were determined by the m-lines technique. The active chromophores were oriented by the corona poling technique and the nonlinear optical susceptibilities were determined by the optical second harmonic generation (SHG) technique.

CHEMICAL SYNTHESIS AND MATERIAL PROCESSING

The chemical structure of used chromophores is shown in Figure 1. Two novel chromophores were synthesized and grafted on polyurethane:

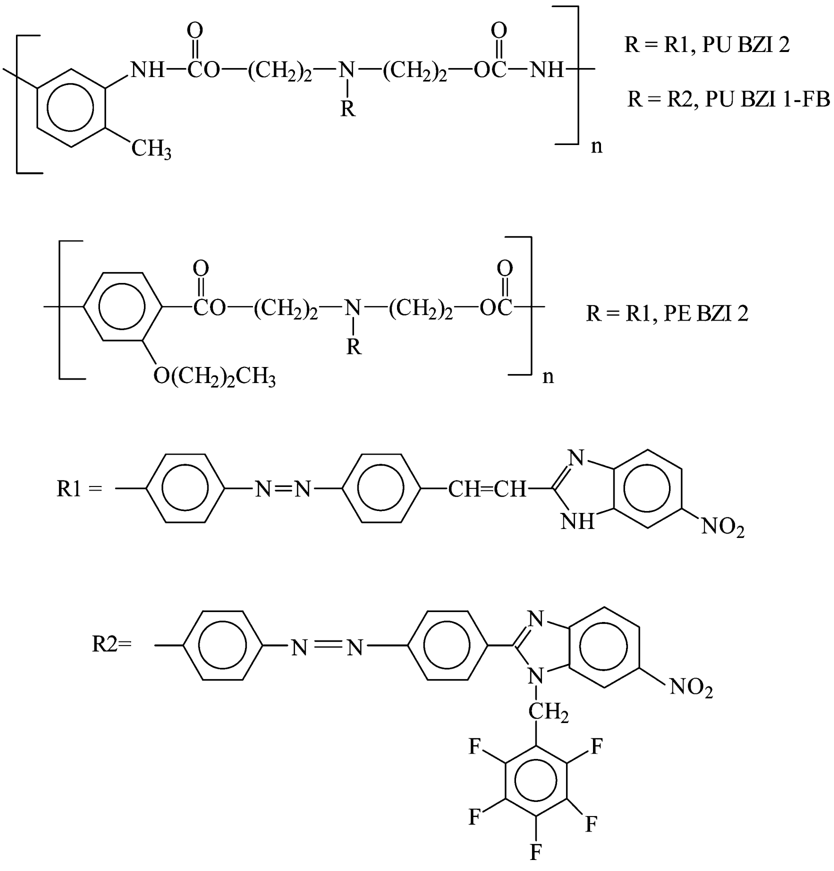

FIGURE 1 Chemical structures of the copolymers.

PU BZI 1-FB and PU BZI 2. For the sake of comparison the chromophore BZI 2 was grafted on polyester. The chemical structures of these novel homopolymers are presented in Figure 1.

Synthesis of Monomers

The synthesis of BZI 2 chromophore, whose chemical structure is shown in Figure 1, is described elsewhere [9]. The second studied chromophore (BZI 1-F, cf. Fig. 1) was synthesized in the following steps:

2-Pentafluorobenzylamino-4-Nitroaniline

2-amino-4-nitroaniline (6 g, 39.2 mmol) was dissolved in 30 mL DMF. K_2CO_3 (10.650 g, 78 mmol) and pentafluorobenzylbromide (7.1 mL, 47 mmol) were added to the solution and the mixture was stirred at room temperature for 4 days. The inorganic solids were then removed by filtration and the remaining solution was poured into 200 mL water. The system was kept under stirring for 30 min in an ice bath and the formation of a solid occurred. The solid was recovered by filtration, dried in an oven at 100°C and recrystallized by toluene. A yellow crystalline material was obtained. The yield after recrystallization was 63%.

Mp: 169°C.

^{1}H NMR (Acetone, d_6): δ 4.611 (s, 2H); δ 4.929 (s, 1H); δ 5.581 (s, 2H); δ 6.753 (d, 1H); δ 7.490–7.646 (d, 2H).

2-(4-Acetamidophenyl)-1-Pentafluorobenzyl-6-Nitrobenzimidazole

2-pentafluorobenzylamino-4-nitroaniline (8.24 g, 24.7 mmol) and p-Acetamidobenzaldehyde (5.385 g, 24.7 mmol) were refluxed in 40 mL glacial acetic acid for 24 h. The solution was then cooled at room temperature and water was slowly added until the formation of a brown precipitate occurred. The amorphous solid was collected by filtration. The yield was 48%.

^{1}H NMR (Acetone d_6): δ 2.138 (s, 3H); δ 5.996 (s, 2H); δ 7.739–7.858 (m, 4H); δ 8.198 (dd, 1H, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz); δ 8.505 (d, 1H, $J = 1.8$ Hz); δ 9.509 (s, 1H).

2-(4-Aminophenyl)-1-Pentafluorobenzyl-6-Nitrobenzimidazole

2-(4-Acetamidophenyl)-1-pentafluorobenzyl-6-nitrobenzimidazole (5.268 g, 11.9 mmol) were suspended in 13 mL $H_2SO_4 + 100$ mL water. The system was refluxed for 90 min. As the temperature increased the solid dissolved giving a dark red solution. After reflux time the solution was cooled and a NaOH water solution (10% by weight) was added dropwise until the pH was 5. The orange solid formed was recovered by filtration. The yield is 91%:

Mp: 235°C.

^{1}H NMR (DMSO-d_6): δ 4.470 (s, 2H); δ 5.913 (s, 2H); δ 6.801 (d, 2H, J = 7.8 Hz); δ 7.527 (d, 2H, J = 7.8 Hz); δ 7.832 (d, 1H, J = 8.8 Hz); δ 8.183 (d, 1H, 8.8 Hz); δ 8.650 (s, 1H).

1-Pentafluorobenzyl-2-(4-{[4-bis(2-hydroxyethyl) amino]phenylazo}phenyl-6-nitro-benzimidazole (BZI 1-F)

2-(4-Aminophenyl)-1-pentafluorobenzyl-6-nitrobenzimidazole (2.27 g, 5.2 mmol) was placed in a flask containing 20 mL H_2O and 2.7 mL 37% HCl; the suspension was cooled to 0–5°C in an ice-water bath. A solution obtained dissolving $NaNO_2$ (0.470 g, 6.8 mmol) in about 10 mL water was added dropwise to the suspension under stirring. Stirring at low temperature was continued for 60 min after the addition of nitrite solution.

Separately, a water-ethanol solution containing sodium acetate (5.350 g, 6.5 mmol) and bis(2-hydroxyethyl)aniline (0.948 g, 5.2 mmol) was prepared. To this, under stirring, the suspension containing the diazonium salt was rapidly added. Immediately the color of solution turned to orange and in few seconds, an orange precipitated of the azo compound formed. Occasionally during this step a rubber-like solid could formed; the use of an ice-bath and the addition of methanol could help the formation of a filtrable powder. The product was collected by filtration and then recrystallized by glacial acetic acid, obtaining pure **BZI 1-FB** as crystalline orange product. Yield 60%.

Mp: 259°C.

^{1}H NMR (DMSO-d_6): δ 3.576 (s, 8H); δ 4.851 (s, 2H); δ 5.952 (s, 2H); δ 6.874 (d, 2H, J = 9.4 Hz); δ 7.773–7.929 (m, 7H); δ 8.198 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2 Hz)); δ 8.701 (s, 1H).

Physico-Chemical Characterization

The thermal behavior of the compounds was studied by differential scanning calorimetry (Perkin-Elmer DSC-7, nitrogen atmosphere, scanning rate 10 K/min), temperature controlled polarizing microscopy (Zeiss microscope, Mettler FP5 microfurnace) and thermo-gravimetric analysis (TA instruments, air, 10 K/min). X-ray diffraction patterns of polymers were recorded on a flat film camera, using Ni filtered CuKα radiation. Proton NMR spectra were recorded on a Varian XL 200 MHz spectrometer. Inherent viscosity (η_{inh}) of polymer solutions at 25°C was measured with an Ubbelohde viscometer in DMF (concentration was 0.5 g/dL) (see Table 1).

TABLE 1 Physico-Chemical Data of Polymers

Polymers	T_g (°C)	T_d (°C)[a]	η_{inh} (dL/g)[b]
PU BZI 2	192	292	0.14
PE BZI 2	157	286	0.14
PU BZI 1-FB	160	287	0.10

[a] Decomposition temperature taken as the temperature corresponding to 5% weight loss in the thermogravimetric run (10 K/min, air atmosphere).

[b] Measured at 25°C in DMF solution.

Synthesis of Copolymers

Both chromophores were chemically grafted on polyurethane backbone. As already mentioned, the BZI 2 chromophore was attached to polyester chain too. The polymer synthesis was done in the following steps:

2-propiloxyterephthaloyl dichlorides were obtained as previously described [10] as well as dry pyridine and dry N-methyl-2-pyrrolidone. Commercial 2,4-tolylendiisocianate was purified by vacuum distillation and stored under inert (N_2) atmosphere. All polymers were prepared by solution polycondensation. Equimolar amounts of chromophore (BZI 2 or BZI 1-FB) and 2,4-tolylendiisocianate or 2-propiloxyterephthaloyldichloride were dissolved in the solvent (NMP for polyurethanes, NMP/pyridine for polyesters) under stirring in N_2 atmosphere. After 4 h reaction, the mixtures were poured into methanol/water, affording precipitation of the crude polymers. These were dissolved in DMF and reprecipitated in methanol/water (a few drops of a concentrated water solution of $CaCl_2$ were necessary in some cases for the coagulation of the precipitate), recovered by filtration and dried in an oven at 80°C for 2 days. Yields ranged from 68 to 70%. The ^{1}H NMR spectra of the polymers were consistent with the expected structures, as well as analytical data. The synthesis of PU BZI 2 is given in detail as an example.

PU BZI 2: BZI 2 (1 g, 2.12 mmol) and distilled 2,4-tolylendiisocianate (0.368 g, 2.12 mmol) were solved in 2 mL anhydrous NMP and kept at 120°C under stirring in N_2 atmosphere for 4 h. Then the viscous solution was poured dropwise in 50 mL methanol/water (9/1 by volume) solution, affording the precipitation of the crude polymer. After the crude polymer was dissolved in 10 mL DMF and poured once again in a methanol/water solution. The final precipitate was recovered by filtration and dried in oven at 80°C for 2 d. The yield was 70%. The ^{1}H NMR spectra of this polymer was consistent with the expected structure.

Thin Films Preparation

Both polyurethane and polyester based polymers are soluble in dimethyl formamide (DMF). Solutions with concentration of 40g/L polymer were prepared and filtered with 0.45 μm porosity filter before thin film deposition. The silica or glass substrates were very well cleaned and treated with a solution of 0.55% w/w of 3 aminopropyl trimethoxysilane in order to improve the film adherence. This procedure was used because films obtained by spinning on freshly cleaned and untreated substrates were highly inhomogenous.

The films were deposited by spin coating on the treated substrates and than dried in an oven at 80°C for two hours. The film thickness ranged between 50 and 105 nm as measured with a DEKTAK profilometer. The optical absorption spectra of obtained in this way thin films are shown in Figure 2.

In order to obtain thicker films necessary for refractive indices measurements the deposition was made by evaporation of a droplet of solution on a silica substrate. The film thickness ranged in this case from 800 to 8200 nm.

LINEAR OPTICAL PROPERTIES

Refractive Index Dispersion

The ordinary and extraordinary indices of refraction of the studied polymer films were determined by the m-lines technique. The

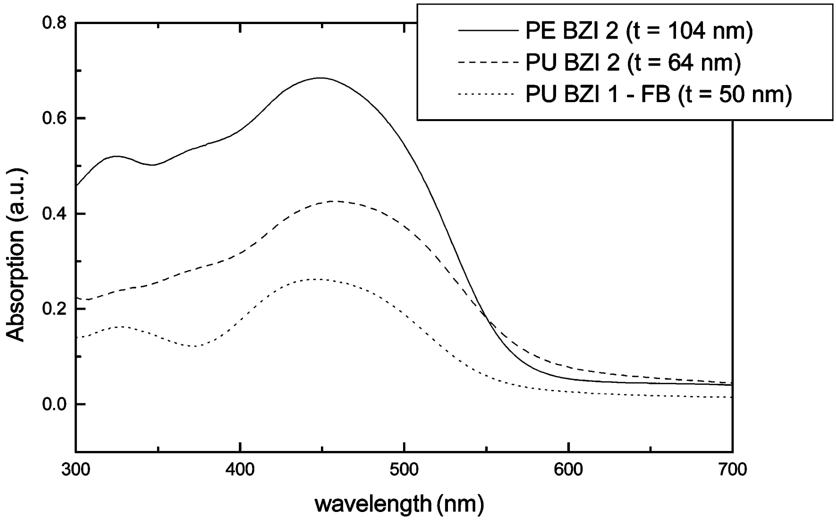

FIGURE 2 Absorption spectra of spun films.

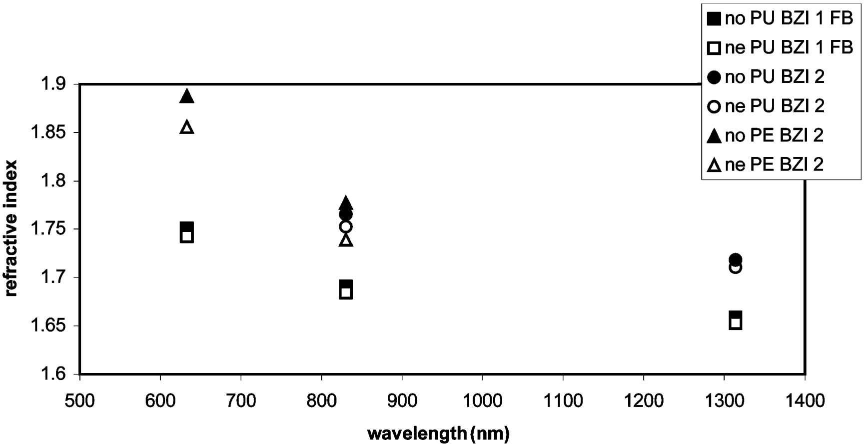

FIGURE 3 Wavelength dependence of ordinary (n_o) and extraordinary (n_e) indices of refraction in thin films of the studied polymers.

measurements were made with a commercial MATRICON PC 2000 Prism coupler equipment and the results are presented in Figure 3.

The polyurethane based films are practically isotropic. A small birefringence is present in polyester based homopolymer with a slightly larger ordinary index of refraction showing a preferential orientation of chromophores and/or polymer chains parallel to the substrate plane. The refractive indices of these polymers are relatively high due to the large density of conjugated phenyl rings. Those of polyurethane PU BZ1 1 FB are slightly lower than for the too other polymers indicating most likely a worse packing.

NONLINEAR OPTICAL PROPERTIES

Kinetic of Corona Poling

Chromophores were oriented by the corona poling technique. The used corona poling set-up is shown schematically in Figure 4. First the polymer films were heated to the glass transition temperature and then a positive DC electric field (tension of 6.0 kV) was applied to the needle electrode leading to corona discharge in surrounding (air) atmosphere. The positive ions are deposed on the poled film creating a large electric field within, which aligns the dipole moments of chromophores preferentially in its direction. In order to find the optimal time for poling the variation of optical absorption spectra was monitored in time. Figure 5 shows, as an example, the absorption spectra

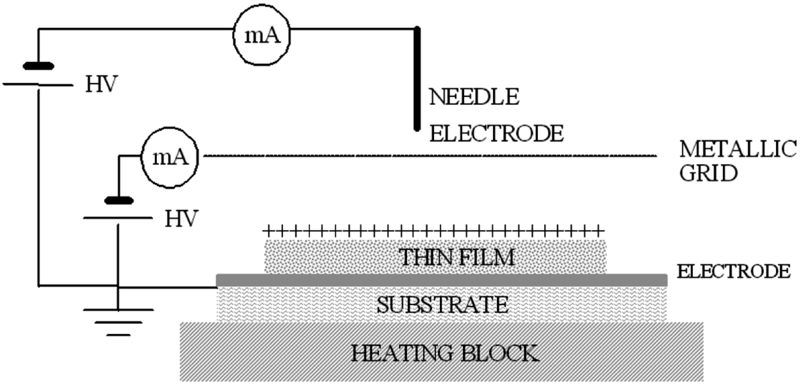

FIGURE 4 Schematic representation of the corona poling set-up.

recorded before and after 1, 2 and 3 minutes corona poling times, respectively, for PE BZI 2 polymer. A typical decrease of the optical density after poling, due to chromophores orientation is observed, with a small shift of the absorption maximum wavelength towards shorter ones. The other two chromophores show a similar behavior. As it can

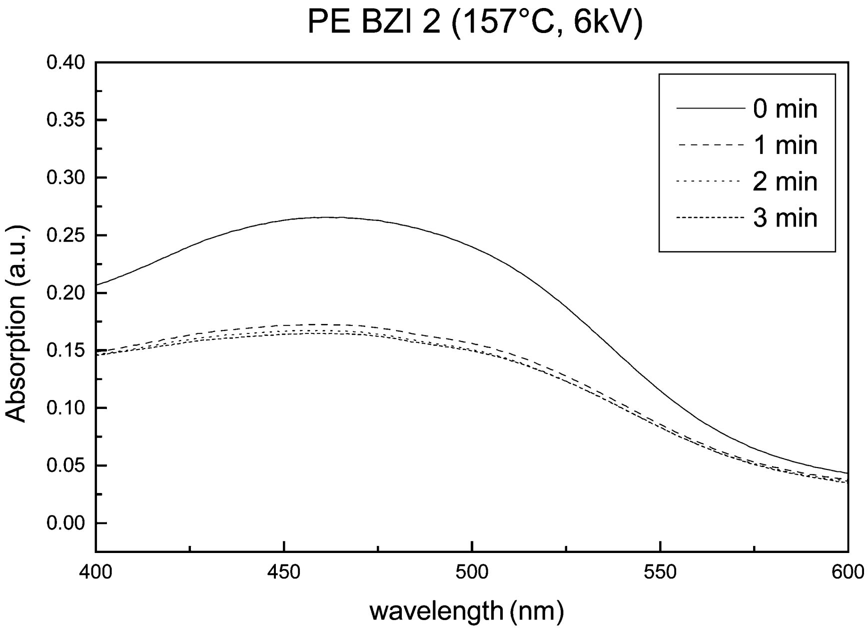

FIGURE 5 Corona poling kinetic for a film of PE BZI 2 (t = 104 nm).

be seen from Figure 5 there is a very little variation of the absorption spectrum for film poled 2 and 3 minutes, showing that the maximum orientation is obtained. Consequently for all further measurements the films were poled for 3 mins at the glass transition temperature. After poling the samples were cooled down to the room temperature and under the applied electric field.

Second Harmonic Generation

The second-order NLO properties of poled films were measured by the optical second harmonic generation technique. Figure 6 shows the experimental set-up used. The light source is a Q switched Nd:YAG laser operating at 1 064.2 nm fundamental wavelength, at 10 pps rate and with 13 ns pulse duration. The harmonic intensity was collected as function of the incidence angle when rotating the sample around an axis perpendicular to the beam propagation direction and coinciding with it.

It is well known that for the symmetry of poled films there are 2 nonzero tensor components: diagonal $\chi^{(2)}_{ZZZ}(-2\omega;\omega,\omega)$ and off diagonal $\chi^{(2)}_{XXZ}(-2\omega;\omega,\omega)$, where Z is direction perpendicular to the thin film substrate. Thus in order to determine both components it is important to be able to change the polarization of the incident wave in a controlled way. This can be done by rotating the half wave plate. The incidence angle dependencies of harmonic intensities were fitted using the corresponding equations for the two polarization configurations (cf. e.g.

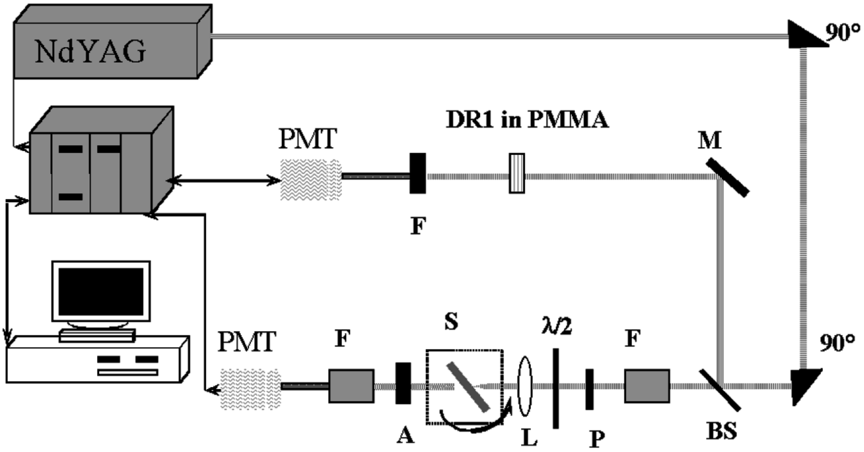

FIGURE 6 Schematic representation of SHG set-up.

TABLE 2 Second Order NLO Susceptibilities for Studied Polymer Films. Details in Text

Chromophore name	Thickness (nm)	d_{sp} (pm/V)	d_{pp} (pm/V)	$a = d_{sp}/d_{pp}$
PEBZI 2	104	2.586	10.719	0.185
			7.808	0.3
PUBZI 2	64	3.841	14.313	0.174
			10.069	0.3
PUBZI 1-BF	50	6.620	20.906	0.204
			16.162	0.3

Swalen and Kajzar [11]) and calibrated with SHG measurements from an α-quartz single crystal plate $\chi^{(2)}_{XXX}(-2\omega; \omega, \omega = 1\,\mathrm{pm/V}[12])$, done at the same conditions.

The two nonzero components for the symmetry of poled films are listed in Table 2. The off diagonal component $d_{sp}(=\frac{1}{2}\chi^{(2)}_{XXZ}(-2\omega; \omega, \omega))$ was determined directly from the s-p fundamental – harmonic beam polarizations configuration measurements. In principle this value should be used to determine the diagonal $d_{pp}(=\frac{1}{2}\chi^{(2)}_{XXZ}(-2\omega; \omega, \omega))$ tensor component. However this procedure led to anomalous d_{pp} values, most likely due to the non adaptability of the free gas model to the studied systems. Therefore we used two approaches. In first we fitted the incidence angle dependence of harmonic intensity by corresponding formula leaving the ratio $a = d_{sp}/d_{pp}$ as a free parameter. In the second approach we put the ratio $a = 3$, as it follows from the free gas model. The d_{pp} values obtained in the first approach are higher as the fit favorizes smaller value of a. The second approach allows to make direct comparisons between different samples.

From Table 2 it is seen that the nonlinear susceptibilities of the studied films are relatively small. This is due, most likely, to the limited poling efficiency at this high chromophore content (homopolymers) and the chromophore aggregation.

Relaxation Study

The relaxation study of the induced polar order was performed by following the variation of the optical absorption spectra and the SHG efficiency in time. An example of such a variation is shown in Figure 7 for a poled film of PE BZI 2. In order to quantify this relaxation we calculated the order ϕ parameter, defined by Eq. (1).

$$\phi = 1 - \frac{A_{pol}}{A_0} \tag{1}$$

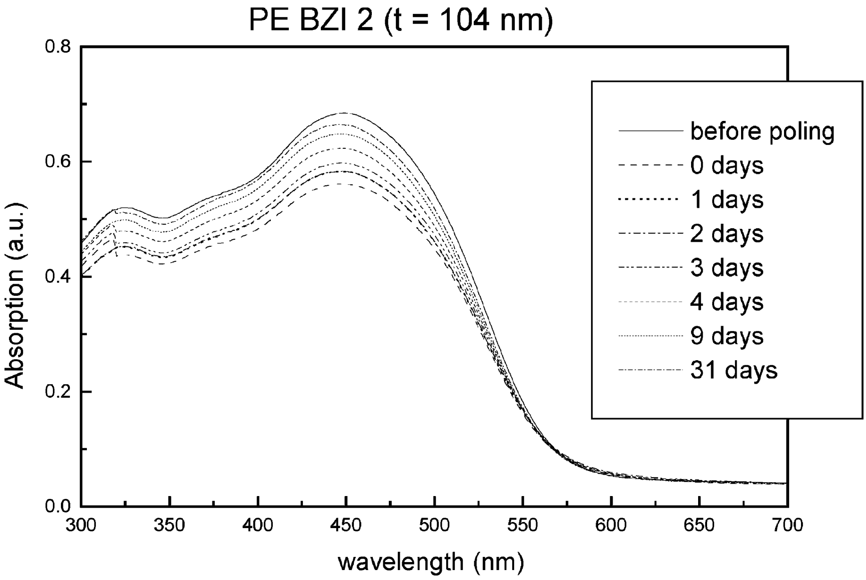

FIGURE 7 Temporal variation of the absorption spectrum for a poled film of PE BZI 2.

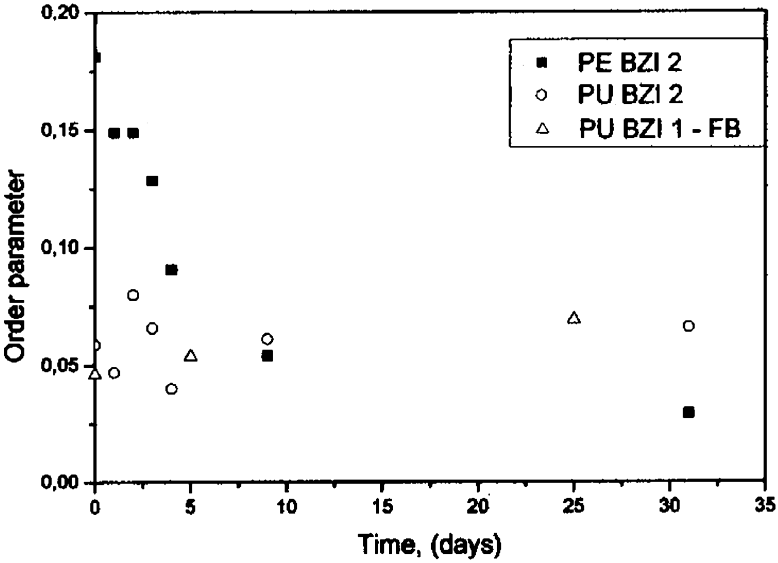

FIGURE 8 Temporal variation of the order parameter ϕ for studied polymers.

where A_0 and A_{pol} are, respectively, the maximum absorbances for before and after poling.

It can be seen that in the case of chromophore PE BZI 2 this relaxation is quite important while in the case of the other two homopolymers almost no relaxation is observed (cf. Fig. 8).

CONCLUSIONS

We have synthesized new NLO active chromophores. The chromophores were grafted on polyurethane and polyester backbones. Both functionalized polymers are soluble and can be processed into thin films. We have characterized their linear and nonlinear optical properties. The present study shows that:

- Homogenous thin films fabrication possible after an adequate substrate treatment.
- The spun polyurethane based films are almost isotropic while the polyester film exhibits a small birefringence.
- The films can be poled by a static electric field. The poling efficiency is not very high, despite the fact that they are resonantly enhanced. This is most likely due to the aggregation problems.
- Concerning the stability of induced polar orientation we observed a fast relaxation in the case of polyester based polymer films and significantly smaller one for the polyurethane based films.

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