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High glass transition chromophore functionalised polyimides for second-order nonlinear optical applications

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Abstract

Nonlinear optical (NLO) polymers with glass temperatures (T_g) as high as 291°C were prepared, PI 2-4 by covalent bonding of a chromophore to the backbone of hydroxyl polyimides via a Mitsunobu reaction, PI 1 as a donor-embedded polyimide was synthesised by polycondensation of a diaminochromophore and 4,4′-(hexafluoroisopropylidene) diphthalic anhydride in a two-step reaction. Poled films of the polymers were measured for their second-harmonic generation (SHG) effect and showed d_{33} values up to 20 pm/V. Some of the films show a stable nonlinear optical response even to 90% of remaining NLO-intensity at 125°C during 200 h. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimides; Nonlinear optics; Stability

1. Introduction

Synthesis and characterisation of organic materials for the use in second-order nonlinear optical (NLO) applications (e.g. second harmonic generation and electrooptic devices) are currently receiving considerable attention [1]. Particularly side-chain polymers have drawn great interest, but the relaxation of the aligned dipoles at high temperature is a major drawback to be overcome. Poled order stability at high temperature is crucial and can be achieved in crosslinked systems [2,3] or by the design of high glass-transition temperature (T_g) polymers like polyimides [4–10] or maleimide-based polymers [11–14]. In this paper, we report the synthesis and nonlinear optical behaviour of a 'donor embedded' side chain polyimide and three side-chain functionalised polyimides. The stability of the nonlinear response was monitored at 125°. Some of the systems investigated show excellent thermal stability.

2. Experimental part

2.1. Materials and instrumentation

All reagents were purchased from Aldrich Chemical Co. and Acros Organics. Reagent grade solvents were dried when necessary and purified by distillation.

The glass transition and decomposition temperatures were measured with a DSC-7 apparatus from Perkin–Elmer with a heating rate of 20°C/min; typically the second run was taken for measuring the T_g. The decomposition temperature was estimated as the intercept of the leading edge of the thermal decomposition peak by the baseline of each DSC scan.

Gel permeation chromatography (GPC) measurements were done with a Waters apparatus with a tunable absorbance detector and a differential refractometer, in tetrahydrofuran (THF) as eluent towards polystyrene standards.

^{1}H nuclear magnetic resonance (NMR) measurements were done with a Bruker 250 MHz and a Bruker 400 MHz apparatus.

2.2. Second harmonic generation measurements

Thin films were obtained by spincoating a solution of the chromophore functionalised poly(imide) polymers in cyclohexanone onto ITO substrates. The spincoated films were carefully dried under vacuum for at least 48 h at a temperature about 10°C below the boiling point of the spincoating solvent. Subsequently they were corona-poled at a temperature approximately 10°C below T_g. The corona-poling set-up consisted of a thin wire, positioned 1 cm above the

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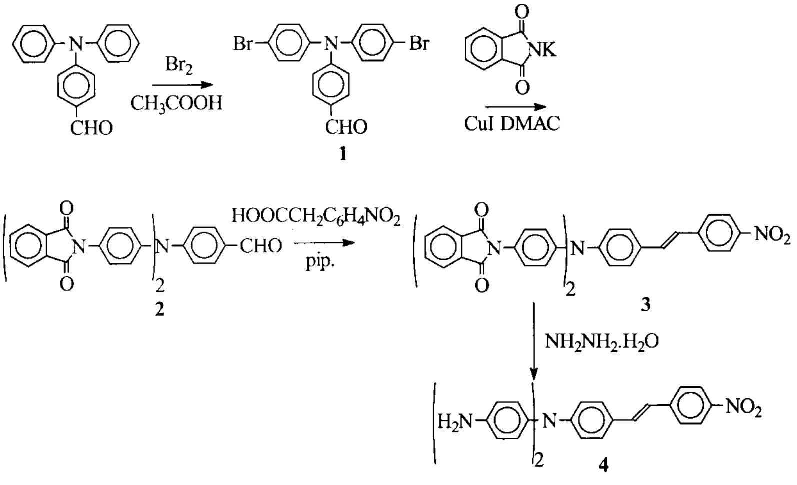


Scheme 1.

polymer film, that was charged to 4–8 kV. The samples were poled for 30 min which gave the best results in terms of SH-efficiency. The second-harmonic coefficient d_{33} was measured using the standard Maker-fringe method [15]. A quartz crystal was used as a reference (d_{11} = 0.3 pm/V) [16] and measurements were done at a fundamental wavelength of 1064 nm. Before each measurement, deposited charges from corona poling were wiped from the surface with methanol. The thermal stability of the NLO response was investigated by heating the corona-poled polymer films to 125°C and following the normalised second-harmonic coefficient $d_{33}(t)/d_{33}(t = 0)$ as a function of time, where $d_{33}(t)$ and $d_{33}(t = 0)$ represent the second-harmonic coefficient at time t and time 0, respectively.

2.3. Synthesis of donor-embedded side chain polyimide *PI 1*

N,N-bis(4-bromophenyl)-4-aminobenzaldehyde (1). To a solution of 5.0 g (18.3 mmol) of 4-diphenylaminobenzaldehyde in 20 ml of acetic acid was added a solution of 5.9 g (36.9 mmol) of bromine in 10 ml of acetic acid. After stirring for 30 min at room temperature 40 ml of water was added and the precipitate was collected by filtration. Recrystallisation from ethanol gives **1** as yellow-green crystals. Yield: 7.6 g (96%), mp 156–156.5°C. ^{1}H NMR (CDCl$_3$, ppm): $\delta = 7.0$ (m, 6H), 7.5 (d, 4H), 7.8 (d, 2H), 9.8 (s, 1H).

N,N-bis(4-phthalimidophenyl)-4-aminobenzaldehyde (2). 2.0 g (4.6 mol) of *N,N*-bis(4-bromophenyl)-4-aminobenzaldehyde **1**, 2.1 g (11.4 mmol) of potassium phthalimide and 4 g (21 mmol) of dry copper(I)iodide was refluxed for 24 h in 30 ml of dry dimethylacetamide under inert atmosphere. After cooling the reaction mixture was diluted with chloroform and filtered. The filtrate was washed with water and dried over MgSO$_4$. After filtration the solvent was evaporated and the residue was purified by column chromatography (silicagel) eluent chloroform. Yield of compound **2**: 1.8 g (69%), mp 280–283°C. ^{1}H NMR (CDCl$_3$, ppm): $\delta = 7.23$ (d; 2H), 7.33 (d; 4H) 7.44 (d; 4H) 7.77 (d; 2H) 7.82 (m; 4H) 7.98 (m, 4H) 9.8 (s; 1H).

N,N-bis(4-phthalimidophenyl)-4-[2-(4-nitrophenyl)-ethenyl] benzeneamine (3). 2.0 g (3.6 mol) of *N,N*-bis(4-phthalimidophenyl)-4-aminobenzaldehyde **2**, 0.8 g (4.4 mmol) of 4-nitrophenyl acetic acid and a few drops of piperidine were heated for 5 h at 115°C in 10 ml of pyridine. After evaporation of the pyridine the residue was purified by column chromatography (silicagel) eluent acetonitrile/chloroform. (3/97, v/v). Yield: 0.8 g (33%), mp 212°C. ^{1}H NMR (CDCl$_3$, ppm): $\delta = 7.07$ (d; 1H), 7.20 (d; 2H), 7.24 (d; 1H), 7.28 (d; 4H), 7.36 (d, 4H), 7.48 2(d; 2H), 7.62 (d; 2H), 7.80 (m; 4H), 7.96 (m; 4H), 8.21 (d; 2H).

Monomer 4 (Scheme 1). 0.80 g (1.17 mmol) of *N,N*-bis(4-phthalimidophenyl)-4-[2-(4-nitrophenyl)-ethenyl]-benzeneamine **3** was dissolved in 20 ml of tetrahydrofuran and purged with argon. 0.3 g (6 mmol) of hydrazine monohydrate was added and the reaction mixture was subsequently refluxed for 5 h. After cooling the reaction mixture was filtered and the precipitate was rinsed by another 100 ml of THF. The combined filtrates were evaporated and the residue was recrystallised from 50 ml of absolute ethanol under inert atmosphere. Yield: 0.35 g (70%), mp 151.8–152.5°C. ^{1}H NMR (CDCl$_3$, ppm): $\delta = 3.6$ (s; 4H), 6.64 (d; 4H), 6.85 (d; 2H); 6.97 (d; 4H), 6.92 (d; 1H), 7.17 (d; 1H), 7.30 (d; 2H), 7.55 (d; 2H), 8.17 (d; 2H).

*Polymer synthesis (**PI 1**).* 0.316 g (0.75 mmol) of monomer **4** and 4 ml of dry 1-methyl-2-pyrrolidinone (NMP) were stirred under inert atmosphere. 0.333 g (0.75 mmol) of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride was added and the solution was kept at room temperature for 48 h. Subsequently a mixture of 0.6 g (7.5 mmol) of dry pyridine and 0.76 g (7.5 mmol) of acetic anhydride was added and the resulting mixture was stirred for another 16 h at room temperature. The polymer solution was diluted with NMP and the polymer was isolated by precipitation in water, filtered and dried. Then redissolved in chloroform, reprecipitated in methanol and dried under vacuum at 90°C for 24 h, yield: 98%.

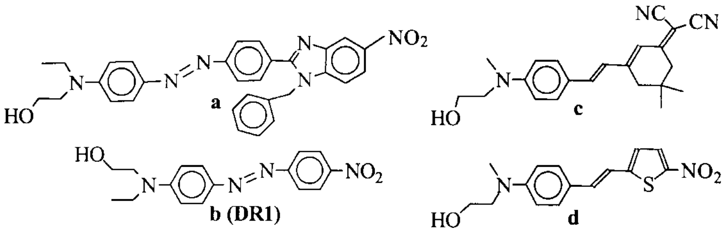


Fig. 1. Structures of chromophores **a**–**d**.

2.4. Synthesis of hydroxyl functionalised precursor polymers *PI 2–4*

PI 2 and **PI 3** were prepared as described in a previous article [5]. **PI 4** was prepared according to a modified procedure from Ref. [17]: 2.13 g (10 mmol) of 4,6-diamino-1,3-benzenediol dihydrochloride[18] in 4 ml of NMP was cooled to 0°C, then 4.44 g (10 mmol) of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride in 10 ml of NMP was added and the resulting mixture was stirred for 10 min. at room temperature. Subsequently 20 ml of dry *m*-xylene was added and water was removed by azeotropic distillation using a Dean-Stark trap. After 4 h of heating at reflux the solution was cooled, diluted with NMP and the polymer precipitated in methanol. The polymer was collected by filtration, redissolved in tetrahydrofuran (THF), reprecipitated in methanol and dried under vacuum at 90°C for 24 h, yield: 53%.

2.5. Synthesis of chromophore *a–d*: Fig. 1

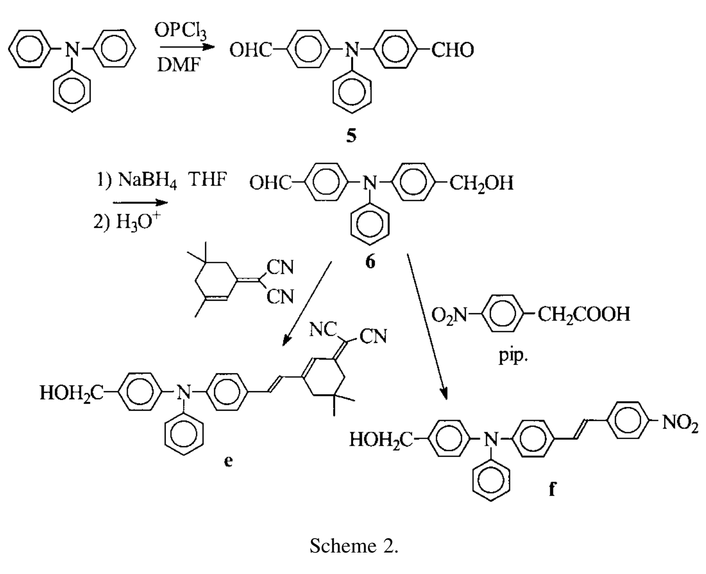
The synthesis of chromophores **a**, **c** and **d** are described in a previous article [5]; chromophore **b** is the commercially available DR1

2.6. Synthesis of chromophore *e* (Scheme 2)

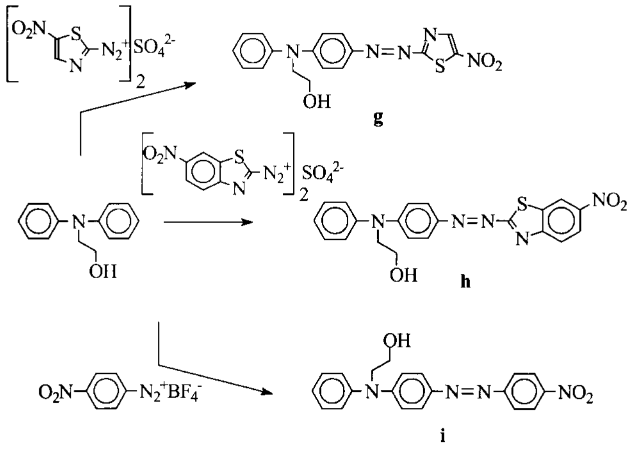
4,4′-Phenyliminobisbenzaldehyde (**5**) was prepared as described in Ref. [19] from 24.5 g (0.10 mol) of triphenylamine in the presence of Vilsmeyer reagent prepared from 32.7 g (0.448 mol) of dimethylformamide and 42 ml of phosphorus oxychloride Yield: 24 g (87%), mp 142°C. ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.1$ (d; 4H), 7.2–7.4 (m; 3H), 7.4 (m; 2H), 7.8 (d; 4H), 9.9 (s; 2H).

*4-[N-phenyl-N-4-(hydroxymethyl)phenyl]aminobenzaldehyde (**6**).* To a solution of 5 g (16.6 mmol) of 4,4′-phenyliminobisbenzaldehyde **5** in 100 ml of dry THF, 0.16 g (4.2 mmol) of sodium borohydride in 5 ml of ethanol was added dropwise under stirring. After stirring for 1 h at room temperature, the reaction mixture was neutralised with diluted hydrochloric acid, extracted with dichloromethane, the extract washed out with water and dried. After filtration the solvent was evaporated and the residue purified by column chromatography (silicagel) eluent dichloromethane/ethylacetate (1/1, v/v). Yield: 3.7 g (73.5%) of a light yellow oil was obtained. ^{1}H NMR ($CDCl_3$, ppm): $\delta =$ 4.7 (s; 2H), 7.0 (d; 2H), 7.1–7.4 (m; 3H), 7.65 (d; 2H), 9.8 (s; 1H).

*Chromophore **e**.* To a solution of 2.4 g (7.9 mmol) of 4-[*N*-phenyl-*N*-4-(hydroxymethyl)phenyl]aminobenzaldehyde (**6**) and 1.47 g (7.9 mmol) of 2-(3,5,5-trimethyl-cyclohex-2-ene-1-ylidene)-1,3-propanedinitrile [20] in 10 ml of dimethyl formamide, 2 ml of acetic acid and 2 ml of piperidine were added. The solution was stirred at room temperature for 1 h, then heated for 8 h at 80°C. After cooling, the reaction mixture was poured in water, filtered, dried and purified by column chromatography (silicagel), eluent dichloromethane/ethylacetate (80/20, v/v) followed by



Scheme 2.



Scheme 3.

recrystallisation from ethanol/water. Yield: 1.6 g (42%) of red crystals, mp 181.2°C. ^{1}H NMR (DMSO-d_6, ppm): $\delta =$ 1.1 (s; 6H), 1.7 (s; 1H), 2.4 (s; 2H), 2.6 (s; 2H), 4.7 (s; 2H), 6.8 (s; 1H), 6.9 (d; 1H), 7.0–7.4 (m; 14H).

*2.7. Synthesis of chromophore **f** (Scheme 2)*

To a solution of 2.5 g (8.3 mmol) of 4[*N*-hydroxymethyl)-phenyl]-aminobenzaldehyde **6** and 1.9 g (10 mmol) of 4-nitrophenylacetic acid in 20 ml of pyridine, a few drops of piperidine were added. The reaction mixture was heated for 3 h under stirring, cooled, poured onto ice, extracted with dichloromethane and dried. After filtration, the solvent was evaporated and the crude reaction product was recrystallised from ethanol. Yield: 1.4 g (40%) of red crystals, mp 74.3°C. ^{1}H NMR ($CDCl_3$ ppm): $\delta =$ 1.7 (t,1H), 4.6 (d; 2H), 7–7.2 (m; 13H), 7.4 (d; 2H), 7.6 (d; 2H), 8.2 (d; 2H).

*2.8. Synthesis of chromophore **g** (Scheme 3)*

2-Amino-5-nitrothiazole 3.5 g (24 mmol) dissolved in 300 ml of acetic acid was cooled to 5°C, then treated by adding dropwise a solution of 1.9 g (27.5 mmol) of sodium nitrite in 200 ml of sulphuric acid under stirring and cooling. After complete addition, the mixture was stirred for 1 h more under cooling, then poured onto ice. The cold mixture was then added to a solution of 5.1 g (24 mmol) of 2-diphenylamino-1-ethanol which itself was prepared from diphenylamine and ethylene oxide under pressure at 240°C [21], in 120 ml of methanol/water 2/1, then stirred for 1 h under cooling after complete addition, followed by neutralisation (pH 5–6) with ammonia and stirred for 1 h more. The precipitate was filtered and recrystallised from aceton/water. Yield of **g**: 0.25 g (2.8%) of purple crystals, mp 189.5°C. ^{1}H NMR ($CDCl_3$ ppm): $\delta =$ 3.8 (t,2H), 3.9 (t; 2H), 6.8–7.4 (m; 4H), 7.6 (s; 1H).

*2.9. Synthesis of chromophore **h** (Scheme 3)*

Reaction of the diazonium salt of 4.7 g (24 mmol) of 2-amino-6-nitrobenzothiazole and 5.1 g (24 mmol) of 2-diphenylamino-1-ethanol under the same reaction conditions as for compound **g**, yielded 0.4 g (4%) of purple crystals, mp 153.7°C. ^{1}H NMR (DMSO-d_6 ppm): $\delta =$ 3.6 (t,2H), 4.0 (t; 2H), 5.0 (t,1 H), 6.9 (d, 2H), 6.9 (d; 2H), 7.35 (m; 3H), 7.5 (m; 2H), 7.9 (d; 2H), 8.1 (d; 2H), 8.3 (dd; 1H), 9.1 (d; 1H).

*2.10. Synthesis of chromophore **i** (Scheme 3)*

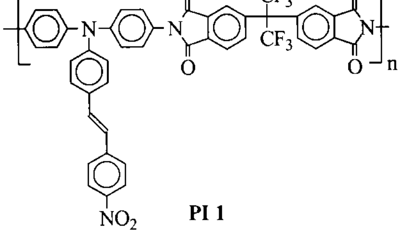
4-Nitrophenyldiazonium tetrafluoroborate 4.7 g (19.8 mmol) and 4.2 g (19.8 mmol) of 2-diphenylamino-1-ethanol were reacted at 0°C for 24 h in dimethylformamide as solvent. The crude reaction product was purified by column chromatography (silicagel). Yield: 0.2 g (3%) of purple crystals, mp149.1°C. ^{1}H NMR ($CDCl_3$ ppm): $\delta =$ 3.9 (t,2H), 4.0 (t; 2H), 6.9 (d; 2H), 7.2 (m; 3H),7.4 (dd; 2H), 7.8 (d; 2H) 8.0 (d; 2H), 8.3 (d; 2H).

*2.11. Chromophore-functionalization of polyimide **PI 2–4***

The general procedure was described in Ref. [5]. Diethylazodicarboxylate (DEAD) was added dropwise to a cooled (0°C) solution of polymer, triphenyl phosphine and hydroxyalkyl chromophore in 25 ml of dry THF. The solution was stirred under inert atmosphere for 24 h at room temperature; then 0.5 ml of methanol was added and stirring was continued for another 24 h. The resulting polymer mixture was diluted with THF and added dropwise to methanol under stirring. The polymer was collected by filtration, reprecipitated twice in methanol out of a THF solution and dried under vacuum.

3. Results and discussion

The synthesis of the "donor embedded" side-chain polyimide **PI 1** (Fig. 2) was a two-step process: polycondensation of monomer **4** with 4,4′-(hexafluoroisopropylidene)-diphthalic anhydride resulted in a poly(amic acid), which was chemically cyclised into its polyimide using a acetic anhydride/pyridine mixture. The keystep for the synthesis of monomer **4** itself was a nucleophilic substition of dibromoderivative **1** with potassium phthalimide in dimethylacetamide and copper(I)iodide as a catalyst. Derivative **2**,



PI 1

Fig. 2. Structure of polyimide **PI 1**.

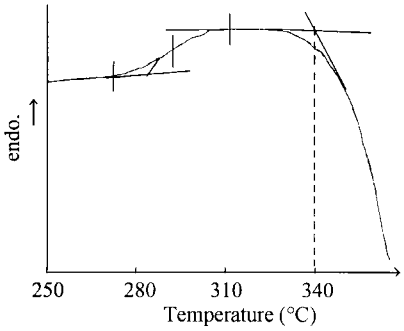


Fig. 3. DSC-plot of polyimide **PI 1**.

is actually a phthalimide-protected diamino-derivative, functionalised with an aldehyde group. This aldehyde group can be easily condensed with various acceptor groups via the Knoevenagel reaction. Deprotection of the phthalimide group with hydrazine results in the formation of the respective monomer. Unfortunately not many acceptor groups are sufficiently stable under the reductive and basic conditions of this final deprotection step, only the nitrostilbene type acceptor was stable enough against hydrazinolysis.

PI 1 is soluble in common organic solvents such as chloroform and THF and the molecular weight was measured by GPC in THF and polystyrene as standards: $\bar{M}_n \times 10^{-4} = 3.5$ (polydispersity 2.1). The glass transition temperature (291°C) was measured with DSC. This T_g is remarkably low in comparison with the T_g of ~350°C of a donor embedded polyimide synthesised by IBM-investigators [8–9]. The only difference between their polyimide and ours is that they used an azo-type chromphore, while we used a stilbene-type chromophore. Apparently this gives a difference in T_g of about 60°C. The degradation temperature (340°C) was estimated by DSC-measurements and was defined as the onset of the first degradation peak as shown in Fig. 3.

Precursor polyimides **PI 2–4** were obtained by polycondensation of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride with 3,3′-dihydroxy-4,4′-diaminobiphenyl, the diamine salt of 2,4-diaminophenol, respectively, 4,6-diamino-1,3-benzenediol. The respective poly(amic acid)s, were thermally cyclised into their polyimide structures. The molecular weights were measured by GPC in THF and polystyrene as standards: **PI 2**, $\bar{M}_n \times 10^{-4} = 2.43$ (polydispersity 1.6); **PI 3**, $\bar{M}_n \times 10^{-4} = 1.37$ (polydispersity 3.9); **PI 4**, $\bar{M}_n \times 10^{-4} = 2.9$ (polydispersity 2.9).

The precursor polyimides were transformed into their chromophore functionalised polyimides via a Mitsunobu reaction [22], by reaction between the pendant hydroxyl groups of the chromophore and the phenol group of the polyimides. The remaining hydroxyl groups of the polymers were reacted with methanol under Mitsunobu conditions. The chromophore content was measured spectrophotometrically.

The structure of the polyimides is presented as follows (Fig. 4). The molecular weights $\bar{M}_n$, polydispersities, T_gs and decomposition temperatures (T_d) are given in Tables 1–3.

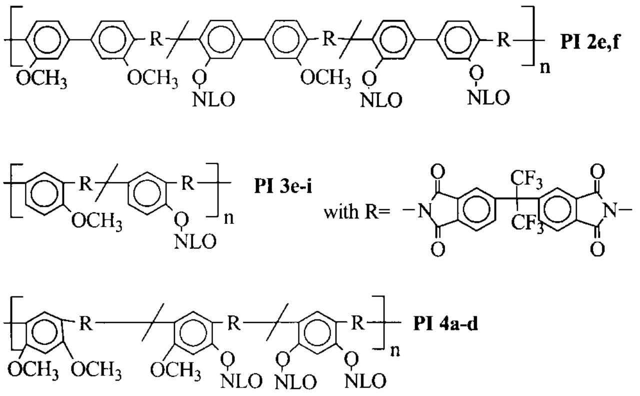


Fig. 4. Structures of functionalised polyimides **PI 2e** and **PI 2f**, **PI 3e–i** and **PI 4a–d**. (Code **a–i** refers to the respective hydroxyalkyl chromophores **a–i**).

The glass transition temperatures of the polymers depend on two factors: (1) the amount of effective functionalisation of the chromophore; and (2) the length of the spacer group by which the chromophore is linked with the polymer backbone. Because of 2 hydroxyl groups per repeating unit in polymer **PI 2** and **PI 4**, the chromophore loading should be higher than with polymer **PI 3**. Although the chromophore

Table 1
Properties of chromophore functionalised **PI 2e** and **f**

Polymer	wt% (max)[a]	$\bar{M}$n[b] (10^4 g· mol^{-1})	D[c]	T_g (°C)	T_d[d] (°C)
PI 2e	30(59)	2.9	2.0	281	> 350
PI 2f	33(56)	0.73	2.2	268	340

[a] Weight percent of NLO-dye in polymer from ^{1}H NMR and spectroscopic measurements (and maximum weight percent).

[b] Apparent molecular weights measured by GPC in THF, polystyrene standards.

[c] Polydispersity: $D = \bar{M}_w/\bar{M}_n$.

[d] Decomposition temperatures.

Table 2
Properties of chromophore functionalised **PI 3e–i**

Polymer	wt%/max[a] (%)	$\bar{M}$n[b] (10^4· g mol^{-1})	D[c]	T_g (°C)	T_d[d] (°C)
PI 3e	29(46)	2.5	3.3	298	> 350
PI 3f	30(43)	2.5	3.2	292	320
PI 3g	32(40)	2.6	2.7	*[e]	254
PI 3h	39(43)	2.4	2.9	252	315
PI 3i	29(39)	2.3	3.2	246	315

[a] Mol% (and wt%) of NLO-dye in copolymer measured from ^{1}H NMR and spectrophotometric measurements.

[b] Apparent molecular weights measured by GPC in THF, polystyrene standards.

[c] Polydispersity: $D = \bar{M}_w/\bar{M}_n$.

[d] Decomposition temperatures.

[e] Not detected.

Table 3
Properties of polyimide chromophore functionalised copolymers **PI 4a–d**

Polymer	wt%(max)[a] (%)	$\bar{M}$n[b] (10^4 g· mol^{-1})	D[c]	T_g (°C)	T_d[d] (°C)
PI 4a	55(64)	5.6	2.8	239	272
PI 4b (DR1)	42(52)	5.0	2.9	218	289
PI 4c	45(55)	9.6	2.9	233	320
PI 4d	44(50)	6.4	2.8	* [e]	252

[a] Weight percent of NLO-dye in polymer from ^{1}H NMR and spectrophotometric measurements (and maximum weight percent).

[b] Apparent molecular weights measured by GPC in THF, polystyrene standards.

[c] Polydispersity: $D = \bar{M}_w/\bar{M}_n$.

[d] Decomposition temperatures.

[e] Not detected.

content is not always the achievable maximum it is clear from Tables 1–3 that T_gs of functionalised **PI 2** and **PI 4** are higher than those from **PI 3**. Chromphore **e** and **f** are linked to the polymer with a methylene group, and the other chromophores with an ethyl group; therefore polymers **PI 2e** and **f** and **PI 3e** and **f** possess higher T_gs than the other functionalised polymers.

The degree of functionalisation is good to excellent with most of the chromophores. In the case of chromophores **e** and **f**, the somewhat lower functionalisation is probably due to an unwanted side reaction. Under Mitsunobu conditions a benzyl-type (and an allyl-type) of an alcohol can possibly react with DEAD to give a hydrazine derivative [22–24]. From NMR-data it is clear that this side reaction does not influence the polymer structure itself and in theory a larger functionalisation is possible simply by using a larger excess of alcohol/DEAD/PPh3, although this was not attempted.

The decomposition temperature of the polyimides is mostly related to the chromophore itself. Chromophore **e** and **f** are triphenylamino-substitituted chromophores and these are known for their better thermal stability compared to their dialkylaminophenylderivatives [25,26]. We tried to synthesise comparable azo-type chromophores substituted with an alcohol function (e.g. starting from 4-(diphenylamino)benzenemethanol) and although some publications describe succesfull diazotation reactions on a triphenylamine core [27], in our hands this reaction failed. Diazotation reactions on 2-diphenylamino-1-ethanol on the other hand were successful and resulted in chromophores **g–i**, although the yields were low.

Seven of the eleven polymer systems could be spincoated onto ITO glass substrates, yielding high quality films. The samples were heated under vacuum during several days to remove any residual solvent. The film thickness was measured with a DEKTAK 2 profilometer. Noncentrosymmetry in the polymers was induced by corona poling at a temperature of 10°C below T_g. The SHG results are summarised in Table 4. The polymers have d_{33} values between 1.2 and 20 pm/V (measured at 1064 nm). However since the second harmonic wavelength was 532 nm, which is rather close to the absorption region of all chromophores these values are resonantly enhanced and should be corrected for absorption. Using the two level model [28], we obtained non resonant $d_{33}(0)$ values of 0.1–3.4 pm/V. These values are rather low in comparison with values published in the literature. There are several possible reasons for these relatively low values. In a typical corona-poling experiment, the effective poling field across the polymer film is unknown. Furthermore, the high poling temperatures that we use increase the conductivity of the polymer samples and the thermal randomisation energy, which results in a lower poling efficiency. In addition, the materials used consist of chromophores with only moderate hyperpolarisabilities and chromophore loading levels, which may also partially explain the low d_{33} levels. Restricted mobility of the chromophores could be another reason. However, most of our systems (except **PI 1**) are simple side-chain polymers with a very typical and expected relaxation behaviour. Hence we do not expect that restricted mobility of the chromophores is the reason for the low second-harmonic coefficients. On the other hand, some of the values of $d_{33}(0)$ that we obtained can be compared with the SHG results for functionalised polyimides we described in Ref. [5]. The absolute value of the second-harmonic

Table 4
Wavelength of maximum absorption (λmax) and second-harmonic coefficients d_{33} and $d_{33}(0)$

Polymer	λmax[a] (Nm)	$d_{33}(\omega)$[b] (pm/V)	$d_{33}(0)$[c] (pm/V)
PI 1	423	3.3	1.0
PI 2e	548	4.0	0.1
PI 2f	436	1.2	0.3
PI 3f	434	3.4	1.0
PI 3I	472	20	3.4
PI 4a	446	9.0	2.2
PI 4b	487	2.4	0.3

[a] Measured in spincoated films.

[b] Measured at 1064 nm.

[c] Extrapolated to zero frequency using the frequency factor $(\omega_{eg}^4)/(\omega_{eg}^2 - 4\omega^2)(\omega_{eg}^2 - \omega^2)$ (obtained from the two level model, with ωeg the frequency of the charge transfer band of the chromophore and ω the excitation frequency) [29].

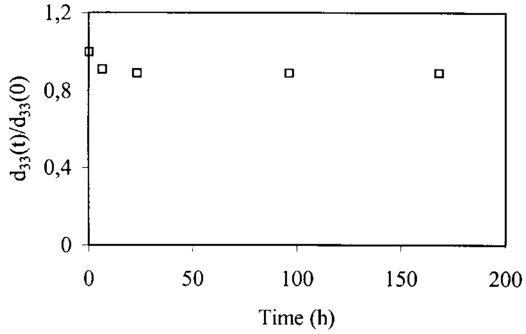


Fig. 5. Plot of the normalised second-harmonic coefficients as a function of time at 125°C of polymer **PI 1**.

efficiency however is not the only factor that is important for polymers in order to be useful in the field of electro-optics and photonics.

One of the motivations to synthesise these high T_g chromophore functionalised polyimide systems was the expectation that these materials would exhibit high stability at elevated temperatures, which is very important for their practical application in optical devices.

A plot of $d_{33}(t)/d_{33}(t=0)$ as a function of time, where $d_{33}(t)$ and $d_{33}(t=0)$ represent the second-harmonic coefficient at time t and time 0, respectively, versus time at 125°C is shown in Figs. 5–7.

It can be seen that after an initial decrease (20 h), the second-harmonic efficiency does not significantly change over a period of 200 h of heating. The 'donor-embedded' polyimide **PI 1** shows an extremely high poled-order stability with 90% of remaining NLO-effect.

From the original value of the optical response of polymers **PI 4a** and **PI 4b**, 69%, respectively 40%, of the polymers **PI 3i** and **PI 3f**, 83% respectively 70% of the second harmonic signal remained. Polyimides and copolyimides studied by Yu et al. [10] gave 85% of remaining nonlinear effect this at 150°C respectively 180°C. Our polyimides **PI 4a**, **PI 3i** and **PI 3f** may be compared for their order stability with the former ones. These results show a high stability for the thermoplastic non-crosslinked systems and these materials are therefore promising for potential applications.

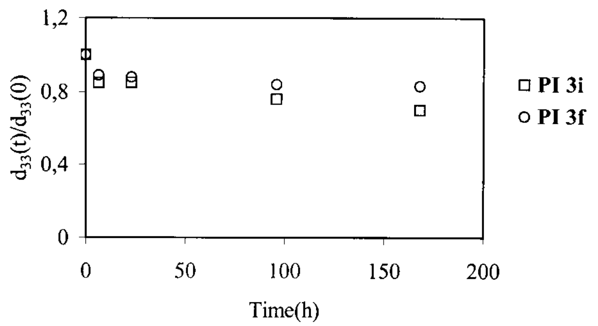


Fig. 6. Plot of the normalised second-harmonic coefficients as a function of time at 125°C of polymer **PI 3I** and **PI 3f**.

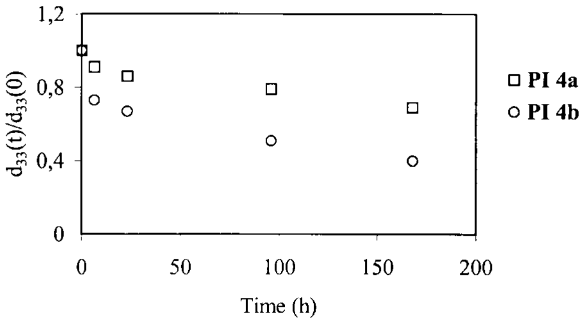


Fig. 7. Plot of the normalised second-harmonic coefficients as a function of time at 125°C of polymer **PI 4a** and **PI 4b**.

4. Conclusion

We synthesised a new "donor-embedded" side chain polyimides as well as new chromophore-functionalised polyimides by functionalisation of the respective hydroxyl polyimide polymers with hydroalkyl chromophores by the Mitsunobu reaction. The polymers exhibit high glass transition temperatures 218–298°C, which result in a stable NLO-response at elevated temperatures. Polyimide **PI 1** lost only 10% of its nonlinearity after 200 h heating at 125°C. In addition the magnitude of the NLO-response suggests that these polymers could be used for NLO-applications.

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