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Polymer 43 (2002) 1581–1585

polymer

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Chromophore-functionalised polymides with high-poling stabilities of the nonlinear optical effect at elevated temperature

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Received 19 August 2001; accepted 9 October 2001

Abstract

Functionalised second-order nonlinear optical (NLO) polyimides have been developed. The key challenge in our approach was a one-step synthesis of these polymers, by reaction of di(hydroxyalkyl) chromophores and diimides utilising the Mitsunobu reaction. Glass transition temperatures in the range of 205–224°C were obtained. Thin spincoated films of the polymers were corona-poled and analysed by second-harmonic generation; values for d_{33} of 30 pm/V were obtained. Poled order stability measurements over periods of 210–500 h resulted in 70–90% of remaining NLO-response at 125°C. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimides; Nonlinear optics; Second-harmonic generation

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1. Introduction

Polymers with high second-order nonlinear optical (NLO) properties are of considerable interest for the development of high-speed light modulators and switches. In order to be useful in optical device applications, the NLO-response should be stable at elevated temperatures [1]. A major drawback is to overcome the relaxation of the aligned chromophores at high temperatures, which can be achieved in crosslinked systems [2,3] or by the design of high glass transition polymers like polyimides [4–19] or maleimide-based (co)polymers [20–23]. The aim of this investigation is an alternative and more convenient method for the design of NLO-polyimides, by a one-step reaction between di(hydroxyalkyl) chromophores and diimide under Mitsunobu [24] conditions. In this way, regularly structured polyimides with high glass transition temperatures and stable NLO-properties can be expected.

2. Experimental part

2.1. Materials and instrumentation

All reagents were purchased from Aldrich 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 as eluent towards polystyrene standards.

^{1}H Nuclear magnetic resonance (NMR) measurements were done with a Bruker 300 MHz apparatus.

2.2. Second-harmonic generation measurements

Spincoated thin films (from cyclohexanone solution onto ITO-coated glass substrate) of the chromophore-functionalised polyimide polymers were carefully dried under vacuum during at least 48 h at a temperature about 10°C below the boiling point of the spincoating solvent. They were corona-poled [1] and the second-harmonic coefficient d_{33} was measured using the standard Maker-fringe method [25]. A quartz crystal was used as a reference ($d_{11} = 0.3$ pm/V) [26] and measurements were done at the fundamental wavelength of 1064 nm. Before each measurement, deposited charges from corona poling were wiped

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PII: S0032-3861(01)00678-4

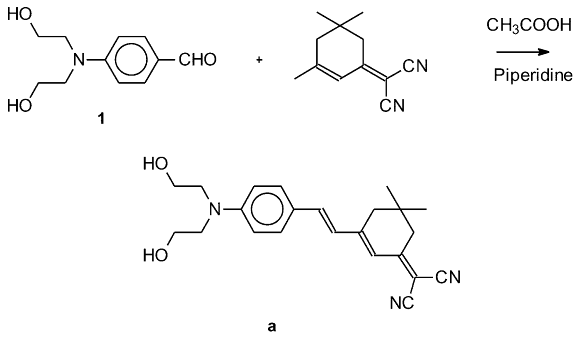

Fig. 1. Synthesis of chromophore *a*.

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 0, respectively.

2.3. Synthesis of chromophore a: Fig. 1

A mixture of 4 g (19.1 mmol) of 4-[*N*,*N*-di(2-ethanol)-amino]benzaldehyde (**1**) (which itself was prepared from diethanolamine and 4-fluorobenzaldehyde in the presence of K_2CO_3 in DMSO solution), 3.6 g (19.1 mmol) of 2-(3,5,5-trimethylcyclohex-2-ene-1-ylidene)-1,3-propanedinitrile, 2 ml of piperidine, 1 ml of acetic acid in 20 ml of *N*,*N*-dimethylformamide was stirred at room temperature for 2 days. The reaction mixture was poured into iced water, extracted with dichloromethane, washed with water, and then the organic phase was dried. After filtration and evaporation of the solvent, the crude reaction product was purified by column chromatography (silicagel).

Yield: 3 g (42%), m.p. 149–152°C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.08$ (s; 6H), 2.46 (s; 2H), 2.59 (s; 2H), 3.60 (t; 4H), 3.83 (t; 4H), 6.67 (d; 2H), 6.77 (s; 1H), 6.82 (d; 1H), 7.03 (d; 1H), 7.41 (d; 2H).

2.4. Synthesis of chromophore b: Fig. 2

2.4.1. 4-[bis(acetoxyethyl)amino]-4′-nitrostilbene (2)

A mixture of 7.3 g (25 mmol) of 4-[bis(2-acetoxyethyl)-amino]benzaldehyde, 6.7 g (37 mmol) of 4-nitrophenyl acetic acid and 2 ml of piperidine was stirred and heated at 115°C. The crude reaction product was purified by column chromatography (silicagel) and was obtained as an oil.

Yield: 3.7 g (36%), ^{1}H NMR ($CDCl_3$, ppm): $\delta = 2.05$ (s; 6H), 3.65 (t; 4H), 4.26 (t; 4H), 6.77 (d; 2H), 6.89 (d; 1H), 7.16 (d; 1H), 7.46 (d; 2H), 7.55 (d; 2H), 8.17 (d; 2H).

2.4.2. Chromophore b

Three and half grams (8.5 mmol) of 4-[bis(acetoxyethyl)-amino]-4′-nitrostilbene (**2**) was treated with a solution of 7 g (0.175 mol) of sodium hydroxide in 70 ml of water and heated at 90°C for 16 h. After cooling, the reaction mixture was neutralised with hydrochloric acid. The precipitate was filtered, recrystallised from ethanol and further purified by column chromatography (silicagel).

Yield: 1.5 g (45.7%), m.p. 182.3–183°C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 3.61$ (t; 4H), 3.87 (t; 4H), 6.72 (d; 2H), 6.95 (d; 1H), 7.23 (d; 1H), 7.40 (d; 2H), 7.59 (d; 2H), 8.19 (d; 2H).

2.5. Synthesis of chromophore c and d: Fig. 3

The procedure of Dalton and co-workers [4] was followed, by reaction of *N*-phenyldiethanolamine and the diazonium salt prepared from 25 mmol of the respective amines and yielded 4.6 g (64.7%) of *c*, m.p. 207.8–209.3°C, respectively, 4.3 g (57.3%) of *d*, m.p. 199.7–201.9°C, ^{1}H NMR of *c* ($CDCl_3$, ppm): $\delta = 3.80$ (t; 4H), 3.90 (t; 4H), 6.90 (d; 2H), 7.90 (m; 4H), 8.30 (d; 2H), ^{1}H NMR of *d* ($CDCl_3$, ppm): $\delta = 2.80$ (s; 3H), 3.70 (t; 4H), 3.90 (t; 4H), 6.70 (d; 2H), 7.70 (d; 1H), 7.90 (d; 2H), 8.00 (m; 2H).

2.6. Synthesis of chromophore e: Fig. 4

A stirred suspension of 11.8 g (0.1 mol) of 4-aminobenzonitrile in a mixture of 23.6 ml of concentrated hydrochloric acid and 75 ml of water was treated dropwise at 0–5°C with a solution of 7.6 g (0.11 mol) of sodium nitrite in 14 ml of water. To the stirred diazonium salt solution, 18.1 g (0.1 mol) of *N*-phenyldiethanolamine in 40 ml of glacial acetic acid was then added slowly under stirring, maintaining the temperature below 5°C. After complete addition, the reaction mixture was stirred for another 30 min at the same

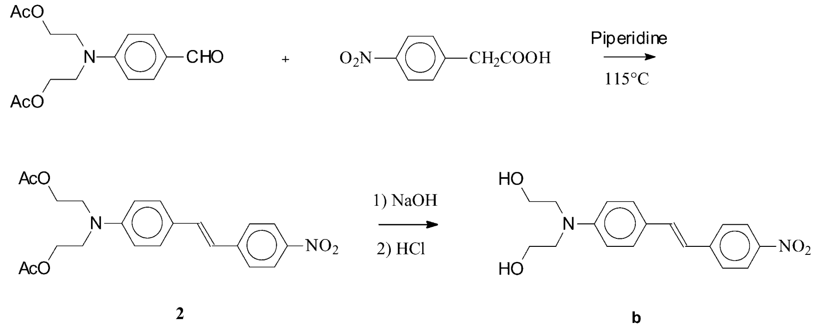

Fig. 2. Synthesis of chromophore *b*.

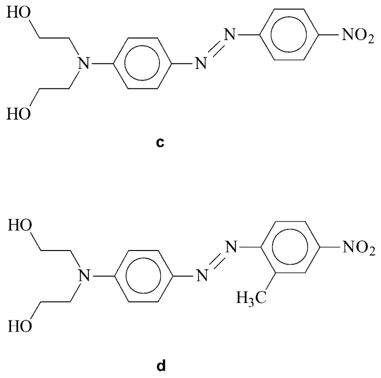

Fig. 3. Structure of chromophores *c* and *d*.

temperature. By addition of 20% of sodium hydroxide, the azo compound was precipitated. The temperature was raised to room temperature and kept for 30 min at this temperature. The precipitate was filtered off, washed with water and recrystallised from methanol. A second purification was done by column chromatography (silicagel).

Yield: 16.7 g (54%), m.p. 173.2–174.5°C, ^{1}H NMR (CDCl$_3$, ppm): $\delta = 3.60$ (m; 8H), 4.95 (t; 2H), 6.91 (d; 2H), 7.80 (d; 2H), 7.90 (d; 2H), 8.00 (m; 2H).

*2.7. Synthesis of 4,4′-(hexafluoroisopropylidene)diphthalimide (**3**)*

4.44 g (4 mmol) of 4,4′-(hexafluoroisopropylidene)-diphthalic anhydride was mixed with 0.09 g (6 mmol) of urea and heated in a round bottom flask at 240°C for 1 h. After cooling the solid was pulverised and heated at 270°C for 1 h. The cooled reaction product was washed out with water, dried and recrystallised from ethanol.

Yield: 3.1 g (70%), m.p. 364.3–366.5°C, ^{1}H NMR (DMSO, ppm): $\delta = 7.62$ (s; 2H), 7.80 (d; 2H), 7.97 (d; 2H), 11.6 (s; 2H).

2.8. Polymer synthesis: Fig. 5

General procedure: To a solution of 1 mmol of 4,4′-(hexafluoroisopropylidene)diphthalimide (**3**), 1 mmol of chromophore diol (*a–e*) and 1.5 mmol of triphenylphosphine in super dry tetrahydrofuran under inert atmosphere, 1.5 mmol of diethylazodicarboxylate was added dropwise under stirring and cooling. The solution was stirred for 3 days at room temperature and the polymer precipitated in methanol. The isolated polymer was dried and fractionated by adding methanol to a tetrahydrofuran solution under stirring. The highest molecular weight fraction was separated and dried under vacuum.

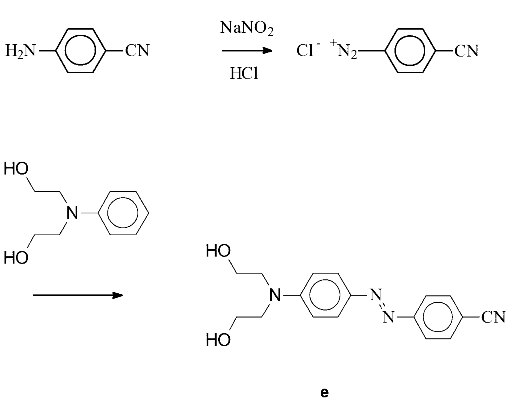

Fig. 4. Synthesis of chromophore *e*.

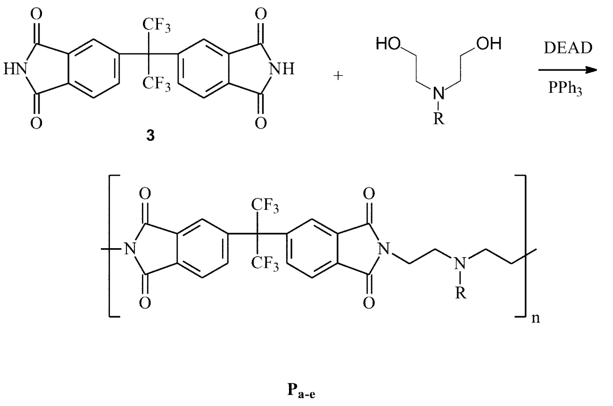

Fig. 5. Synthesis of polymers P$_{a-e}$ (code *a–e* refers to the respective bis-(hydroxyalkyl) chromophores *a–e*).

3. Results and discussion

The synthesis of chromophore-functionalised polymers was a one-step process. The reaction of di(hydroxyalkyl) chromophores and diimide under Mitsunobu conditions gives raise to direct formation of the polyimide structure. This alternative route has several advantages compared to the classical methods. Like there are:

(a) a two-step process of dialkylamino chromophore and bisanhydride, where di(hydroxyalkyl) chromophore has to be transformed into dialkylamino chromophore under Mitsunobu conditions which results in a reaction mixture that is difficult to separate in pure material with fairly low yields,
(b) functionalisation of precursor polyimides with hydroxyalkyl chromophore resulting in random and not complete functionalisation,
(c) synthesis of donor embedded polyimides, where the harsh conditions of the chromophore monomer preparation leads to some restrictions of the chromophore structure.

The method presented here is a fast, direct and elegant procedure to obtain chromophore-functionalised polyimides and because of the mild conditions there are no restrictions for the kind of chromophore to be incorporated into the polymer structure.

Table 1
Synthesis and properties of chromophore-functionalised polyimides PI_{a-e}

Polymer	wt%[a]	$\bar{M}_w$[b] (10^4 g/mol)	D[c]	T_g (°C)	T_d[d] (°C)
PI_a	44	0.93	1.6	224	280
PI_b	40	2.04	1.5	219	296
PI_c	40	1.58	1.6	210	251
PI_d	41	1.26	1.6	205	248
PI_e	38	1.63	1.7	213	254

[a] Weight percent of NLO-dye in polymer.

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

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

[d] Decomposition temperature.

Table 2
Wavelength of maximum absorption (λ_{max}) and second-harmonic coefficients $d_{33}(\omega)$ and $d_{33}(0)$

Polymer	λ_{max}[a] (nm)	$d_{33}(\omega)$[b] (pm/V)	$d_{33}(0)$[c] (pm/V)
PI_a	489	12	1.5
PI_b	427	13	3.9
PI_c	454	11	2.4
PI_d	456	13	2.9
PI_e	431	30	8.6

[a] Measured in spincoated films.

[b] Measured at 1064 nm.

[c] Extrapolated to zero frequency using the frequency factor $\omega_{eg}^4/[(\omega_{eg}^2 - 4\omega^2)(\omega_{eg}^2 - \omega^2)]$.

The structure of the synthesised polyimides PI_{a-e} is given in Fig. 5 whereas code *a–e* refers to the respective hydroxyalkyl chromophores *a–e*.

The molecular weights $\overline{M}_n$, polydispersities D, glass transition temperatures T_gs, decomposition temperatures T_d as well as weight percent of chromophore unit and yields are given in Table 1.

From the results, it is seen that fairly high (70.9%) to very high yields (95.0%) of polymer are obtained. However, because of rather high polydispersities 3.8–6.0, the polymers were fractionated.

The glass transition temperatures are between 205 and 224°C and may be compared with the results obtained for polymers with the chromophore linked to the polyimide backbone this for analogues chromophores [10,11,14,15].

Furthermore, the decomposition temperatures are 41–77°C higher than the respective glass transition temperatures. Hence, thermal stability of the NLO-response can be expected. The chromophore load 38–44 wt% is comparable and even higher than in the case of side-chain polyimides [10,11,14].

Here, we obtain fully chromophore functionalised units and a regularly structured polymer.

The incorporation of fluoro groups is to improve the solubility so to obtain good optical quality films.

The polymers could be spincoated from cyclohexanone solution onto ITO glass substrates, yielding high quality films except for PI_a. 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 polymer films was induced by corona poling at a temperature 10°C below T_g.

The second-harmonic generation (SHG) results are summarised in Table 2. The polymers have d_{33} values between 11 and 30 pm/V (measured at 1064 nm of induced light). The relationship $d_{33}/d_{31} \approx 3$ was observed for all polymers. This leads to the assumption that the NLO-chromophores are Boltzmann-distributed in the poling field, and the poling was achieved in a low poling field limit [27]. Since the second-harmonic wavelength was 532 nm which is rather close to the absorption region of the chromophores, the values d_{33} are resonantly enhanced and must be corrected for absorption. Using the two level model [28] nonresonant values of 1.5–8.6 pm/V were obtained. These values may be compared with those obtained for chromophore-functionalised polyimides described in the literature [5,12,13,29]. The motivation for the design of these high T_g chromophore-functionalised polyimides was the expectation that these materials will exhibit high NLO-stability at elevated temperatures because of stabilised dipole orientation, which is very important for their use in optical device applications. To evaluate the high-temperature stability, we studied the temporal stability of the SHG effect, by plotting $d_{33}(t)/d_{33}(t=0)$ as a function of time, where $d_{33}(t)$ and $d_{33}(t=0)$ represent the SHG effect at time t and 0, respectively, versus time at 125°C. The results of these measurements are given in Figs. 6 and 7. It can be seen that after an initial decrease of 9–20%, the NLO-response does not significantly change over a period of 210 h for polymers PI_{c-e}. As a result, 76–89% of the initial NLO-response remains after the heat treatment. Heating of PI_b for a period of 500 h at 125°C resulted in 70% of remaining NLO-response.

Our results show extremely high stabilities for noncrosslinked thermoplastics, they may be compared and are even better than the results obtained for polyimides described in the literature [5–7,10,14,15,29–33] where 75–90% of remaining SHG effect was stated. The thermal characteristics indicate that these polymers are useful for device applications.

4. Conclusion

We succeeded in our approach to obtain high T_g polyimides in a one-step process, from di(hydroxyalkyl) chromophore and diimide under Mitsunobu conditions. This method is an elegant procedure to incorporate chromophores, which may be unstable under the harsh conditions by using other approaches for chromophore synthesis. Second-order susceptibility values (d_{33}) up to 30 pm/V were obtained. The polymers exhibit high glass transition temperatures 205–224°C which results in highly stable NLO-response at elevated temperatures; a maximum loss

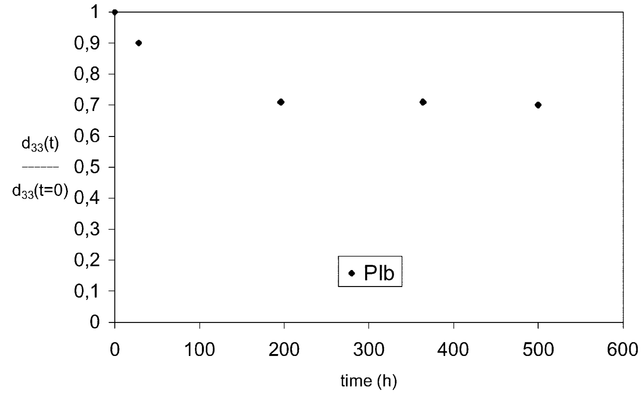

Fig. 6. Plot of the normalised second-harmonic coefficients as a function of time at 125°C of polymer PI_b.

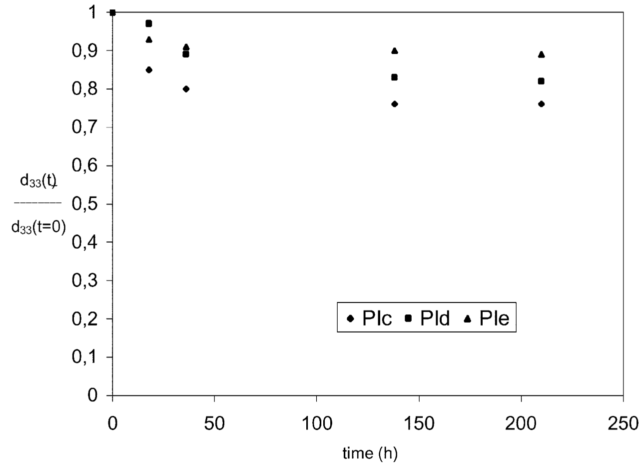

Fig. 7. Plot of the normalised second-harmonic coefficients as a function of time at 125°C of polymers PI_{c-e}.

of 30% was observed after 210 h of heating at 125°C. These thermoplastics are therefore promising materials for the construction of devices.

Acknowledgements

This work was supported by research grants from the Fund for Scientific Research-Flanders (FWO-V, G.0308.96), from the Belgian Government (IUAP P4/11, ‘Supramolecular Chemistry and Supramolecular Catalysis’) and from the University of Leuven (GOA/95/01). E. Gubbelmans is a research fellow from the IWT, T. Verbiest is a postdoctoral fellow of the Fund for Scientific Research-Flanders.

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