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High glass transition chromophore functionalised poly(maleimide-styrene)s for second-order nonlinear optical applications

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Abstract

Nonlinear optical polymers with high glass transition temperatures were prepared by polymer analogous reaction of maleic anhydride copolymers, with aminoalkyl-functionalised azo- and stilbene chromophores. Glass transition temperatures from 178 to 228°C were obtained. Poled films of the polymers were characterised by second-harmonic generation and showed a nonlinear optical response that is stable at elevated temperatures. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Polymers with high second-order nonlinear optical (NLO) properties are of considerable interest for the development of electro-optic and photonic devices. In order to be useful in optical device applications, the second-order response should be stable at elevated temperatures, the NLO-polymers should be chemically and physically stable as well and optical loss has to be minimised [1] The non-centrosymmetry for second-order NLO-materials can be achieved by poling of a polymer film under strong electric field conditions, while heating at a temperature close to its glass transition temperature (T_g). A major difficulty is the long-term relaxation of the NLO-chromophores in the polymer matrix. In order to suppress this reorientation, rigid polymer backbones exhibiting high T_gs were synthesised. This can be achieved either in crosslinked systems [2,3] or by the design of thermoplastics like polyimides [4–9] or maleimide-based polymers [10–18]. In this paper, precursor polymers obtained by radical copolymerisation of maleic anhydride and 2,6-dichlorostyrene, *p*-methoxystyrene or β-methoxystyrene were synthesised. These copolymers were then transformed in their respective chromophore functionalised polymers by reaction with aminoalkyl-functionalised azo- and stilbene chromophores and characterised for their nonlinear optical behaviour. The stability of the nonlinear response was monitored at 125°C for more than 1000 h. 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. Maleic anhydride and 2,2′-azobisisobutyronitrile were purified by crystallisation from chloroform and methanol, receptively. Disperse Red 95% was used as purchased from Aldrich Chemical Co. 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 tuneable absorbance detector and a differential refractometer, in tetrahydrofuran (THF) as eluent towards polystyrene standards.

^{1}H nuclear magnetic resonance (NMR) measurements

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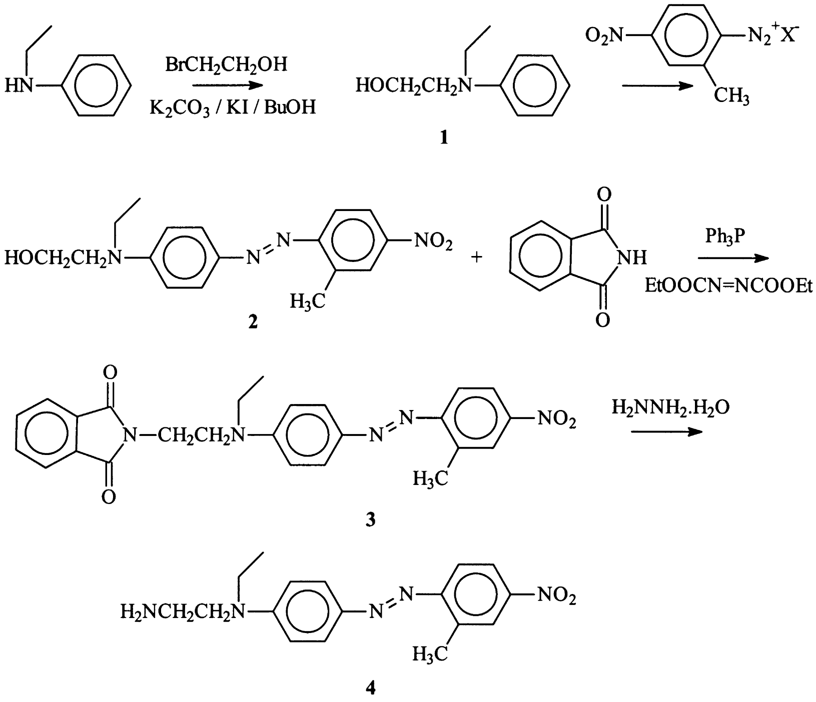


Scheme 1. Synthesis of aminoalkyl chromophore **4**.

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(maleimide styrene) polymers in 1,2,3-trichloropropane 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 and the second-harmonic coefficient d_{33} was measured using the standard Maker-fringe method [19]. A quartz crystal was used as a reference ($d_{11} = 0.3$ pm/V) [20] and measurements were done at the 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 normalized 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.

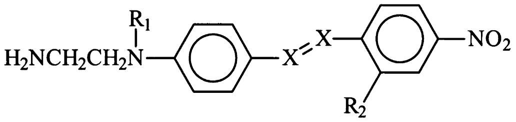
2.3. Synthesis of N-ethyl-N-[4-[(2-methyl-4-nitrophenyl)azo]phenyl]-1,2-ethylene-diamine (4) (Scheme 1)

2-(N-ethyl-N-phenylamino)ethanol (**1**): A mixture of 48.4 g (0.4 mol) of fresh distilled *N*-ethylaniline, 45.6 g (0.36 mol) of 2-bromoethanol, 50 g (0.47 mol) of potassium carbonate, 1.5 g (9 mmol) of potassium iodide in 200 ml of *n*-butanol was refluxed under stirring and argon atmosphere for four days. After cooling, the suspension was filtered, the solvent removed and the residue was distilled under reduced pressure. Yield 42.5%, b.p. 135–140°C (1 mmHg).

N-ethyl-N-[4-(2-methyl-4-nitrophenyl)azo]phenyl]aminoethanol (**2**): A stirred suspension of 30.4 g (0.2 mol) of 2-methyl-4-nitroaniline in a solution of 52 ml of concentrated hydrochloric acid in 200 ml of water was treated dropwise at 0–5°C with a solution of 15 g (0.216 mol) of sodium nitrite in 29 ml of water. 2-(*N*-ethyl-*N*-phenylamino)ethanol 33 g (0.2 mol) in 10 ml of glacial acetic acid was then added slowly, maintaining the temperature below 5°C, and the mixture was stirred for another 30 min after complete addition. The azo compound was precipitated by the addition of 20% sodium hydroxide and left for 30 min at room temperature. The precipitate was filtered off, washed with water and recrystallised from methanol. Yield 45% m.p. 148–150°C.

N-ethyl-4-[2-methyl-4-nitrophenyl)azo]-N-(2-phthalimidoethyl)aniline (**3**): To a solution of the alcohol (**2**) (15.35 g, 46.8 mmol) in 1-methyl-2-pyrrolidinone (55 ml) and tetrahydrofuran (120 ml), 18.4 g (70.2 mmol) of triphenylphosphine and 10.3 g (70.2 mmol) of phthalimide was added. A solution of diethyl azodicarboxylate (12.3 g, 70.2 mmol) in 60 ml of THF was then added dropwise to this solution. The resulting mixture was stirred overnight. After evaporation of the THF, the residue was purified by column chromatography (silicagel). Yield of compound **3**: 46.3%, m.p. 195.3–198.6°C.

Synthesis of amine (**4**): To a solution of 6 g (13 mmol) of compound **3** in 150 ml of THF, 1.6 g (32.5 mmol) of



5: X=N, R_1=CH_3, R_2=CH_3
6: X=N, R_1=Et, R_2=H
7: X=CH, R_1=CH_3, R_2=H

Fig. 1. Structures of aminoalkyl chromophore **5**–**7**.

hydrazine hydrate was added. The mixture was refluxed for 5 h under argon and then cooled to room temperature, filtered and the precipitate washed out with THF. The THF solution was evaporated to dryness, the reaction product was then purified by column chromatography (silicagel). Yield of compound **4**: 34%, m.p., 125–126.4°C, ^{1}H NMR ($CDCl_3$, ppm): $\delta = 1.35$ (s; 2H), 1.50 (s; 3H), 2.70 (s; 3H), 3.60–3.90 (m; 6H), 6.90 (d; 2H), 7.20–8.00 (m; 3H), 8.20 (m; 2H).

2.4. Synthesis of amine (**5**)–(**8**)

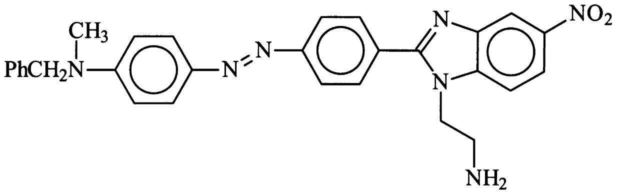
All other amine functionalised chromophores were synthesised according to the same procedure: a chromophore-alcohol was transformed into its phthalimido- derivative via the Mitsunobu reaction [21] and subsequently reacted with hydrazine to give the amine (Fig. 1).

Amine **5**: Following an analogous procedure as for amine **4**. Yield 39.2%, m.p. 94.6°C, ^{1}H NMR ($CDCl_3$) $\delta = 1.35$ (s; 2H); 2.70 (s; 3H), 3.10 (s; 3H), 3.20 (m; 4H), 6.90 (d; 2H), 7.20–8.00 (m; 3H), 8.20 (m; 2H).

Amine **6**: Starting from Disperse Red 1: Yield 18.3%, m.p. 119.7–120.3°C, ^{1}H NMR ($CDCl_3$,, ppm) $\delta = 1.35$ (s; 2H), 1.40 (t; 3H), 3.60–3.90 (m; 6H), 6.90 (d; 2H), 7.20–8.00 (m; 4H), 8.20 (d; 2H).

Amine **7**: Starting from chromophore-alcohol described in the literature [22]. Yield 83.3%, m.p. 164.4–166.2°C, ^{1}H NMR ($CDCl_3$,, ppm) $\delta = 1.35$ (s; 2H), 3.18 (s; 3H), 3.20 (m; 4H), 6.80 (d; 2H), 7.05 (d; 1H), 7.38 (d; 1H), 7.45 (d; 2H), 7.53 (d; 2H), 8.43 (d; 2H).

Amine **8**: Following the procedure given in the literature [16]. Yield 53.7%, m.p. 192–194°C, ^{1}H NMR ($CDCl_3$,, ppm) $\delta = 1.35$ (s; 2H), 3.20 (s; 3H), 4.30 (t; 2H), 4.70 (s; 2H), 6.80–8.70 (m; 16H). (Fig. 2)



8

Fig. 2. Structure of aminoalkyl chromophore **8**.

2.5. Polymer synthesis

Three precursor polymers were synthesised by copolymerisation of maleic anhydride and 2,6-dichlorostyrene (**PCl**), *p*-methoxystyrene (**Pp**), β-methoxystyrene (**Pβ**) respectively in 1,4-dioxane as a solvent with 1 wt% of 2,2′-azobisisobutyronitrile at 65°C for 24 h under inert atmosphere, in 50:50 mole ratio. The copolymers were isolated by precipitation in methanol, filtered and dried under vacuum.

The chromophore-functionalised polymers were obtained by reaction of the respective precursor copolymers and aminoalkyl chromophore in 1-methyl-2-pyrrolidinone

General procedure for the functionalisation: To a solution of 0.5 mmol of repeating unit of copolymer in 15 ml of 1-methyl-2-pyrrolidinone, 0.5 mmol of aminoalkyl chromophore was added under stirring and the reaction mixture was kept at room temperature for 24 h. Then 40 ml of a solution of acetic anhydride/pyridine (2:1 v/v) was added at room temperature, stirring was continued for 1 h, then the solution was heated at 60°C for 12 h. After cooling, the chromophore functionalised polymers were isolated by precipitation in methanol, filtered and dried. This procedure was repeated twice. The composition of the obtained copolymers was evaluated by ^{1}H NMR.

3. Results and discussion

The synthesis of the chromophore-functionalised polymers was a two step process. Maleic anhydride precursor copolymers with 2,6-dichlorostyrene, *p*-methoxystyrene, and β-methoxystyrene were transformed into their respective chromophore functionalised poly maleic(amic acid) copolymers and subsequently transformed into their respective maleimide copolymers by a smooth reaction with pyridine/acetic anhydride at 60°C. The general reaction scheme of the synthesis of these chromophore-functionalised poly(maleimide styrene)s is given in Scheme 2 (Synthesis of chromophore functionalised poly(maleimide

Table 1
Properties of poly(maleimide-2,6-dichlorostyrene) chromophore functionalised copolymers **PCl 4**–**8**

Polymer	M_{pol} (wt%)[a]	$\bar{M}_n$ (10^4 g mol^{-1})[b]	D[c]	T_g (°C)	T_d (°C)[d]
PCl-4	36 (40.7)	1.00	2.98	–[e]	254
PCl-5	36 (42.4)	1.39	2.07	189	284
PCl-6	36 (42.4)	1.18	2.92	195	242
PCl-7	36 (41.1)	1.15	2.77	206	275
PCl-8	36 (54.8)	1.12	2.52	206	235

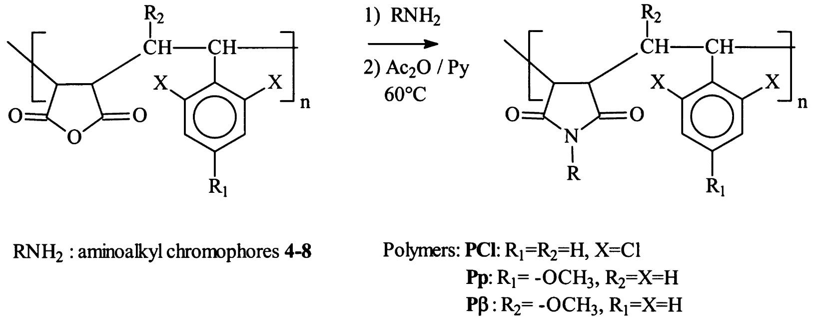
[a] Mol (and Weight) percent of NLO-dye in copolymer measured from ^{1}H NMR and spectrophotometric measurements.

[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.



Scheme 2.

styrene)s (code numbers refer to the respective amine chromophores)).

The copolymers are soluble in 1-methyl-3-pyrrolidinone, dimethylformamide and cyclohexanone. The mol percentages of the NLO-unit in the copolymers, molecular weights $\bar{M}_n$, polydispersities (D), T_gs and decomposition temperatures (T_d) are given in Tables 1–3.

From these results we see an incorporation of 36 mol% of the maleimide unit in the poly(maleimide-2,6-dichlorostyrene)copolymers while in the *p*- and the β-methoxystyrene copolymers 50 mol% is incorporated; here we obtained alternating copolymers. The glass transition temperatures (T_gs) are between 178 and 228°C and are comparable to those of other stable polymers used in the field of nonlinear optics [10–15]. The rigidity of the main chain leads to high glass transition temperatures, which is a prerequisite for useful nonlinear optical materials. Hence thermal stability of the NLO-response can be expected.

Seven from the eleven polymer systems could be spin-coated from a 1,2,3-trichloropropane solution onto ITO glass substrates, yielding high quality films. While **PCl-4** and **5**, **Pp-5** and **Pβ-5** gave bad optical quality films and could not be used for second-harmonic generation and relaxation measurements. 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 4 and 66 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, we obtained non resonant $d_{33}(0)$ values of 1.1–12.5 pm/V. The ratio d_{33}/d_{31} was always ≈3 for all polymers.

Relatively high off-resonant values were obtained for **PCl-8** and **Pβ-8** with the nitrobenzimidazole as chromophore. For copolymers **PCl-6** and **Pp-6**; **Pp-4** and **Pβ-4** one would expect similar $d_{33}(0)$ values because all these polymers contain similar azobenzene dyes with comparable concentrations. The difference in observed d_{33}-values can probably be attributed to differences in effective poling field strength (a parameter usually unknown in corona-poling experiments). The rather low value for **PCl-7** can be explained by the relatively low hyperpolarizability of the stilbene unit (as compared to the azobenzene and nitrobenzimidazole dyes) incorporated in the polymer.

The d_{33} values we obtained are higher than those given in the literature by Sung et al. [12] obtained for poly(*N*-azodye)maleimide-styrene copolymers, where they observed d_{33} values of 3–5 pm/V (1064 nm), while Chang et al. [13] observed values of 16.2 pm/V (1064 nm) for *N*-phenyl maleimide-methylmethacrylate, respectively, styrene copolymers. This authors did not give however nonresonant values ($d_{33}(0)$). Zentel et al. [18] obtained values up to

Table 2
Properties of poly(maleimide-*p*-methoxystyrene) chromophore functionalised copolymers **Pp 4–6**

Polymer	M_{pol} (wt%)[a]	$\bar{M}_n$ (10^4 g mol^{-1})[b]	D[c]	T_g (°C)	T_d (°C) [d]
Pp-4	50 (44.4)	11.11	2.26	–[e]	325
Pp-5	50 (46.7)	12.69	1.52	178	253
Pp-6	50 (46.7)	11.81	2.53	203	261

[a] Mol (and Weight) percent 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 poly(maleimide-β-methoxystyrene) chromophore functionalised copolymers **Pβ 4**,**7**,**8**

Polymer	M_{pol} (wt%)[a]	$\bar{M}_n$ (10^4 g mol^{-1})[b]	D[c]	T_g (°C)	T_d (°C) [d]
Pβ-4	50 (44.4)	0.89	2.18	228	270
Pβ-7	50 (45.3)	0.83	3.53	185	225
Pβ-8	50 (59.0)	0.69	1.65	227	258

[a] Mol (and Weight) percent 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.

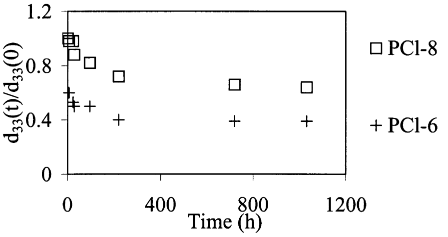


Fig. 3. Plot of the normalised second-harmonic coefficients as a function of time at 125°C of polymers **PCl 6**, **8**.

100 pm/V (1064 nm) this for *N*-substituted maleimide-vinyl urethane copolymers, while Günter et al. [15] obtained d_{31} values of 23 pm/V (1064 nm) for *N*-substituted maleimide-styrene copolymers; no nonresonant values were given.

The absolute value of the second-harmonic 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 polymaleimide 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 $d_{33}(t)/d_{33}(t=0)$, 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. 3 and 4. It can be seen that after an initial decrease, the second-harmonic efficiency does not significantly change over a period of 1000 h of heating. From the original value of the optical response in polymer **Pp-6**, 76% of the second-harmonic signal remained. The other systems initially show a larger decrease in the NLO-response and stabilise to 64, 63 and 54% for **PCl-8**, **Pβ-4** and **Pp-4**, respectively, while **PCl-6** stabilises at 39% of the original value of the optical response.

Compared to stability measurements obtained by Sung et al. [12], who measured 20% remaining optical response after 18 h at 130°C and Günter et al. [15], who measured a decrease of 20% of the original SHG value after 10 min of heating at 80°C this for *N*-substituted maleimide-styrene copolymers, our polymaleimide systems show much higher poling stabilities. Our results show that poly (maleimide-styrene)s are promising candidates for practical applications.

Table 4
Wavelength of maximum absorption (λ_{max}) and second-harmonic coefficients (d_{33} and d_{31}) of poly maleimide chromophore functionalised copolymers

Polymer	λ_{max} (nm)[a]	$d_{33}(\omega)$ (pm/v)[b]	$d_{33}(0)$ (pm/V)[c]
PCl-6	478	64.0	9.9
PCl-7	435	4.0	1.1
PCl-8	442	28.8	7.4
Pp-4	466	42.0	7.9
Pp-6	477	25.0	3.9
Pβ-4	469	28.6	4.4
Pβ-8	439	66.0	12.5

[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 ω_{eg} the frequency of the charge transfer band of the chromophore and ω the excitation frequency) [23].

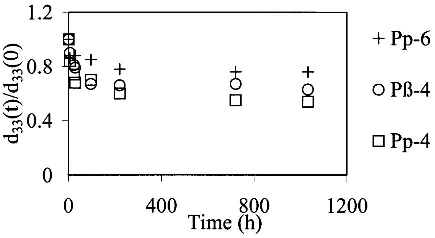


Fig. 4. Plot of the normalised second-harmonic coefficients as a function of time at 125°C of polymers **Pp 4**, **6** and **Pβ 4**.

4. Conclusion

We synthesised chromophore functionalised poly maleimide copolymers by reaction of poly maleic anhydride precursor polymers with aminoalkyl functionalised azo- and stilbene chromophores. The polymers exhibit high glass transition temperatures 178–228°C which results in stable NLO-response at elevated temperatures. For example one of our polymer systems lost only 24% of its nonlinearity after 1000 h of heating at 125°C. In addition the magnitude of the NLO-response suggests that these polymers could be useful for NLO-applications.

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