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Poly(N-phenylmaleimide)- and poly(N-biphenylmaleimide)-urethanes, functionalised with NLO-phores for second-order nonlinear optical applications

Wim Ballet [a], Thierry Verbiest [b], Marcel Van Beylen [a], André Persoons [b], Celest Samyn [a,*]

[a] *Laboratory of Macromolecular and Physical Organic Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium*

[b] *Laboratory of Chemical and Biological Dynamics and Center for Research on Molecular Electronics and Photonics, Katholieke Universiteit Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium*

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Abstract

Nonlinear optical (NLO) polymers with high glass transition temperatures were prepared by polymer analogous reaction of methyl vinylisocyanate copolymers, with hydroxyalkyl-functionalised chromophores which results into urethane linkages between the chromophore and the polymer backbone. The precursor polymers show an alternating structure and glass transition temperatures from 211°C to 247°C were obtained.

Poled films of the polymers were characterised by second-harmonic generation measurements. Stability of the NLO effect of 85% can be obtained at elevated temperatures.

Keywords: Polymaleimide copolymers; Nonlinear optics; Polyurethanes

1. Introduction

Nonlinear optical (NLO) materials with high and stable second-order NLO properties are of great importance for the development of electro-optic and photonic devices. Organic and polymeric materials with high polarisable π-electronic systems can exhibit large NLO response [1–4] and possess several advantages over inorganic substances such as $LiNbO_3$, KH_2PO_4, etc. [5]; high resistance to laser damage, fast response times, low dielectric constants, ease in processing and architectural modification for optimising optical nonlinearities. Oriented polymers are therefore especially attractive for NLO studies. A major problem is the long-term relaxation of the NLO chromophore incorporated in the polymer systems. In order to suppress the reorientation, photo- as well as chemical crosslinkable systems were investigated [6–16]. Another approach is the synthesis of polymers exhibiting high T_g's (glass transition temperatures), this by the design of thermoplastics like polyimides [17–22] or maleimide-based polymers [23–30] which possess a rigid polymer backbone. In two previous papers [31,32] poly(maleimide-styrene)s functionalised with NLO-phores were investigated; some of these materials showed a high and stable NLO response after a prolonged time (2000 h) at 125°C. In this paper, precursor polymers obtained by radical polymerisation of N-phenyl- or N-biphenylmaleimide and methyl vinylisocyanate were synthesised. The copolymers were then transformed in their poly(maleimide-urethane) copolymers by reaction with hydroxyalkyl-functionalised chromophores and characterised for their NLO behaviour.

* Corresponding author. Tel.: +32-16-327438; fax: +32-16-327990.

E-mail address: celest.samyn@chem.kuleuven.ac.be (C. Samyn).

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The stability of the NLO response was monitored at 125°C for 500 h.

2. Experimental part

2.1. Materials and instrumentations

Tetrahydrofuran (THF) was dried over sodium potassium alloy and distilled prior to use. All other starting materials were purchased from Acros Organics or Aldrich Co. and used without purification unless stated otherwise.

The glass transition and decomposition temperatures were measured with a DSC-7 apparatus from Perkin Elmer with a heating rate of 10°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 base line of each DSC scan.

Gel permeation chromatography measurements were done with a Waters apparatus with a tunable absorbance detector and a differential refractometer, in 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.

2.2. Second-harmonic generation measurements

Spin-coated thin films (from cyclohexanone onto ITO substrate) of the chromophore-functionalised poly-(maleimide-urethane) copolymers were carefully dried under vacuum during at least 48 h at a temperature about 10°C below the boiling point of the spin-coating solvent. They were corona-poled and the second-harmonic coefficient d_{33} was measured, using the standard Maker-fringe method [33]. A quartz crystal was used as a reference ($d_{11} = 0.3$ pm/V) [34]. The fundamental wavelength of 1064 nm was used. Deposited charges were wiped from the surface with methanol before each measurement. The thermal stability of the NLO response was investigated by heating the corona-poled polymer films at 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 chromophore *1*

A mixture of 3.44 g (0.019 mol) of 4-[*N*-2-(hydroxyethyl)-*N*-methylamino]-benzaldehyde, 3.6 g (0.019 mol) of 2-(3,5,5-trimethylcyclohex-2-ene-1-ylidene)-1,3-propanedinitrile, 4 ml of piperidine, 2 ml of acetic acid and 2 ml of acetic anhydride in 20 ml of *N*,*N*-dimethylformamide was stirred at 80°C for 8 h. After cooling, the reaction mixture was poured in iced water (200 ml). The precipitate was filtered, washed with water and air-dried, then purified by column chromatography (silicagel) using chloroform–ethylacetate (9:1 v/v) as an eluent. Compound **1** was obtained as dark blue–green crystals. Yield 4.1 g (62.5%), m.p. 158–159°C, ^{1}H-NMR (DMSO-d_6) δ (ppm) = 1.01 (s; 6H), 2.52 (m; 4H), 3.01 (s; 3H), 3.47 (t; 2H), 4.71 (t; 2H), 6.72 (s; 1H), 6.73 (d; 2H), 7.10 (d; 1H), 7.23 (d; 1H), 7.53 (d; 2H) (Fig. 1).

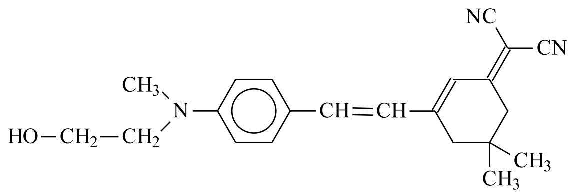


Fig. 1. Strucure of chromophore **1**.

2.4. Synthesis of chromophore *2*

To a cooled solution of 7.8 g (0.04 mol) of 2-amino-6-nitro-benzothiazole in 200 ml of acetic acid, a solution of 2.8 g of sodium nitrite in 200 ml of concentrated sulphuric acid was added under cooling (<10°C) and stirring. This solution was poured onto ice and added to a solution of 7.4 g (0.049 mol) *N*-(2-hydroxyethyl)-*N*-methylaniline in 120 ml of methanol–water (2:1 v/v), this under stirring and cooling. After complete addition stirring was continued for another hour, then the reaction mixture was neutralised with ammonia to pH 5–6. The precipitate was purified by recrystallisation from acetone–water. Further purification was done by column chromatography (silicagel) using chloroform–ethylacetate (9:1 v/v). Compound **2** was obtained as purple crystals. Yield 5.9 g (41%), m.p. 220°C, ^{1}H-NMR ($CDCl_3$): δ (ppm) = 2.8 (s; 3H), 3.20 (t; 2H), 3.5 (t; 2H), 4.10 (s; 1H), 6.90 (d; 2H), 7.40 (d; 1H), 7.90 (d; 2H), 8.10 (d; 1H), 9.10 (s; 1H) (Fig. 2).

2.5. Synthesis of chromophore *3*

A mixture of 15.2 g (0.1 mol) of 2-methyl-4-nitroaniline in 10 ml of concentrated hydrochloric acid and 32 ml of water was treated dropwise under cooling (<5°C) and stirring with a solution of 10.3 g of sodium nitrite in 20 ml of water. After complete addition the

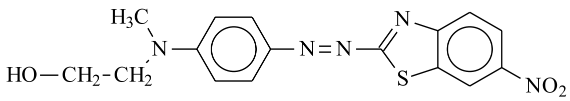


Fig. 2. Structure of chromophore **2**.

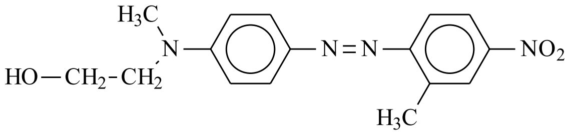


Fig. 3. Structure of chromophore **3**.

solution was stirred for 1 h more at 0–5°C. To the diazonium salt solution, 15.1 g (0.1 mol) of *N*-(2-hydroxyethyl)-*N*-methylaniline in 6 ml of acetic acid was added slowly and after complete addition stirred for another hour under cooling. After neutralisation (20% NaOH), the precipitate was washed with water and recrystallised from methanol–water. After a second purification by column chromatography (silicagel), compound **3** was obtained as orange crystals. Yield 16 g (51%), m.p. 145–146°C, ^{1}H-NMR ($CDCl_3$) δ (ppm) = 2.70 (s; 3H), 3.20 (s; 3H), 3.70 (t; 2H), 4.10 (q; 2H), 6.80 (d; 2H), 7.60 (d; 1H), 7.90 (s; 2H), 8.1 (m; 2H) (Fig. 3).

2.6. Synthesis of chromophore 4

This compound was prepared as described in a previous paper [31]. ^{1}H-NMR (DMSO-d_6) δ (ppm) = 3.19 (s; 3H), 3.80 (m; 2H), 4.49 (t; 2H), 4.76 (s; 2H), 5.10 (t; 1H), 6.90 (d; 2H), 7.25–7.38 (m; 5H), 7.82 (d; 2H), 7.92 (d; 2H), 8.08 (d; 2H), 8.21 (dd; 1H), 8.59 (d; 1H) (Fig. 4).

2.7. Monomer synthesis

N-phenylmaleimide and *N*-biphenylmaleimide were synthesised from maleic anhydride and the corresponding amine by a two-step procedure, the polymaleimide-carboxylic acid intermediate was prepared first in ether solution under reflux for 1 h. The isolated amide-acid was then transformed into the respective functionalised maleimide by heating on a steam bath in the presence of sodium acetate and acetic anhydride. The purified maleimide showed m.p. 88–89.2°C for *N*-phenylmaleimide respectively 195.6–196.1°C for *N*-biphenylmaleimide.

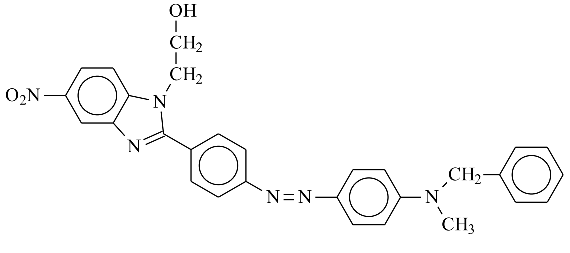


Fig. 4. Structure of chromophore **4**.

2.8. Methyl vinylisocyanate

78 g (1.2 mol) of sodium azide was dissolved in 280 ml of water and cooled to −10°C, then 84 g (0.8 mol) of methacryloylchloride in 280 ml of xylene was added at a temperature <5°C. After complete addition, the mixture was stirred for another hour. The organic layer was separated, washed out with a saturated sodium carbonate solution, then twice with water and dried.

The azide solution was then added to 20 ml of xylene at 80°C. After the nitrogen evolution was complete, the isocyanate was distilled (b.p. 69°C).

2.9. Polymer synthesis

General procedure: The copolymerisations were carried out in dioxane solution under argon atmosphere at 65°C in the presence of 1 wt.% of 2,2′-azobisisobutyronitrile for 24 h; 20 mol% excess of methyl vinylisocyanate was used. The resulting polymer solution was cooled then precipitated into diethyl ether under inert atmosphere, filtered and dried under reduced pressure.

Yield : poly(methyl vinylisocyanate)-*alt*-(*N*-phenylmaleimide) : 87% (P1)
poly(methyl vinylisocyanate)-*alt*-(*N*-biphenylmaleimide) : 91% (P3)

2.10. Functionalisation with chromophores – general procedure

The precursor polymer (1 mmol) was dissolved in dry THF (10 ml) whereas 1 or 0.5 equivalent of chromophore alcohol this towards the isocyanate component was added, followed by 0.1 ml of dibutyltin dilaurate. The reaction mixture was heated under inert atmosphere at 60°C under stirring for three days. Then methanol was added and heating was continued for another two days in order to complete the urethane formation. The functionalised polymers are precipitated in methanol, filtered and dried, then redissolved in THF, reprecipitated, filtered and dried. Model polymers were synthesised by the same procedure, by reactions of the prepolymers with methanol. Molecular weights ($\overline{M}_n$) of the respective polymers are: $P_I = 12935$ (*N*-phenyl), $P_{II} = 8543$ (*N*-biphenyl) with polydispersities 3.9 respectively 4.5.

3. Results and discussion

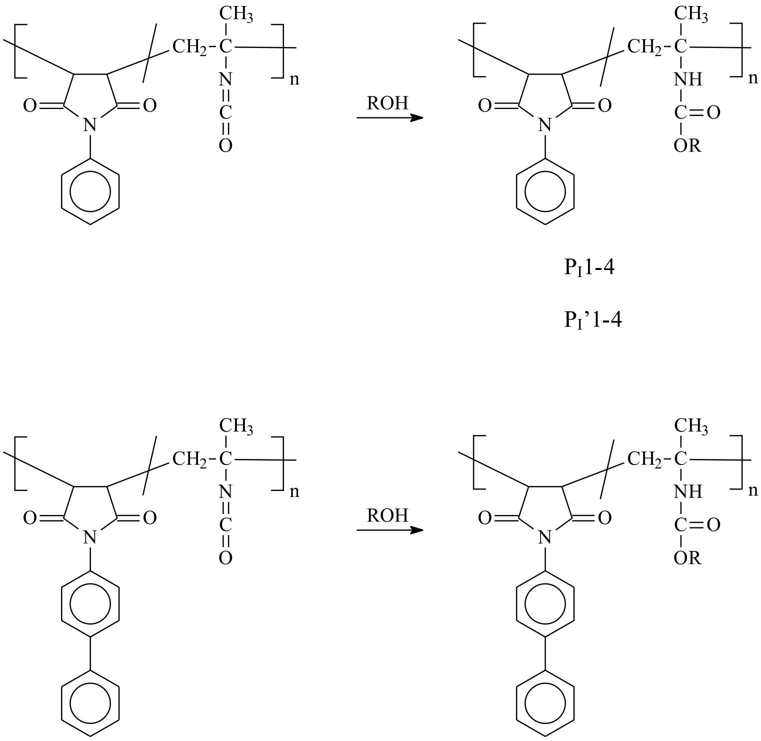
The synthesis of the chromophore-functionalised polymers was a two-step process. The polyisocyanate precursor polymers were obtained by a simple radical polymerisation of methyl vinylisocyanate and a substituted maleimide, which resulted in alternating copolymers. The precursor polymers were transformed into their chromophore-functionalised poly(maleimide-urethane)s, by a polymer analogous reaction of the isocyanate groups with the respective hydroxyalkyl chromophores. In order to complete the functionalisation, methanol was used.

The structure of the poly(maleimide-urethane)s is presented in Scheme 1. The molecular weights $\overline{M}_n$, polydispersities, T_g's and decomposition temperatures (T_d) are given in Tables 1–3. The glass transition temperatures of polymers P_I **1**–**4** are between 231°C and 247°C and of polymers P'_I **1**–**4** between 211°C and 237°C. The difference in T_g's between the two series of copolymers was the degree of functionalisation, a lower degree of functional groups results in higher T_g's for the same chromophores incorporated.

The decomposition temperatures (estimated as the intercept of the leading edge of the thermal decomposition peak by the base line of each DSC scan) are between 8°C and 39°C higher than the respective T_g's. Since poling is typically done 10°C below T_g, significant thermal decomposition is not expected to occur during the poling process. From polymers P_{II} **1**–**4** no T_g could be detected, the decomposition temperatures can be compared with those obtained for P_I and P'_I copolymers.

A reasonable to high chromophore loading level could be obtained for P_I **1**–**4** respectively P'_I **1**–**4**, while for P_{II} copolymers rather a low functionalisation degree was obtained. One of the reasons may be steric hindrance of the additional phenyl group. Furthermore the nonfunctionalised P_{II} copolymer is much less soluble than the P_I copolymer.

Eight polymer systems could be spin coated onto ITO glass substrates, yielding films with good quality. 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 show d_{33} values up to 14.4 pm/V (measured at 1064 nm). Since the second-harmonic wavelength was 532 nm, which is rather close to the absorption region of all chromophores, the values are resonantly enhanced and should



P_I1-4

P_I'1-4

P_{II}1-4

ROH: hydroxyalkyl chromophores 1-4

Scheme 1. Structure of polymers P_I, P'_I and P_{II} **1**–**4** (code **1**–**4** refers to the respective hydroxyalkyl chromophores **1**–**4**).

Table 1
Properties of poly(phenylmaleimide-urethane) chromophore-functionalised copolymers P_I **1**–**4**, 0.25 eq. chromophore alcohol **1**–**4** used

Polymer	Wt.% (max)[a]	$\overline{M}_n$ (10^4 g/mol)[b]	D[c]	T_g (°C)	T_d (°C)[d]
P_I **1**	16 (37.8)	1.35	2.5	247	260
P_I **2**	11.9 (39.3)	[e]	–	242	255
P_I **3**	21 (36.3)	1.14	3.2	231	240
P_I **4**	25 (48)	0.88	3.6	240	255

[a] Weight (and maximum weight) percent of NLO dye in copolymer measured from ^{1}H-NMR.
[b] Apparent molecular weights measured by GPC in THF, polystyrene standards.
[c] Polydispersity: $D = \overline{M}_w/\overline{M}_n$.
[d] Decomposition temperature.
[e] Bimodal.

Table 2
Properties of poly(phenylmaleimide-urethane) chromophore-functionalised copolymer P'_I **1**–**4**, 0.5 eq. chromophore alcohol **1**–**4** used

Polymer	Wt.% (max)[a]	$\overline{M}_n$ (10^4 g/mol)[b]	D[c]	T_g (°C)	T_d (°C)[d]
P'_I **1**	51 (55)	1.16	3.5	211	260
P'_I **2**	42.9 (56.5)	[e]	–	216	[f]
P'_I **3**	48 (53.3)	0.96	5.3	225	245
P'_I **4**	51 (64.8)	0.83	5	237	245

[a] Weight (and maximum weight) percent of NLO dye in copolymer measured from ^{1}H-NMR.
[b] Apparent molecular weights measured by GPC in THF, polystyrene standards.
[c] Polydispersity: $D = \overline{M}_w/\overline{M}_n$.
[d] Decomposition temperature.
[e] Bimodal.
[f] Could not be detected.

Table 3
Properties of poly(biphenylmaleimide-urethane) chromophore-functionalised copolymers P_{II} **1**–**4**, 0.5 eq. chromophore alcohol **1**–**4** used

Polymer	Wt.% (max)[a]	$\overline{M}_n$ (10^4 g/mol)[b]	D[c]	T_g (°C)	T_d (°C)[d]
P_{II} **1**	11 (38.8)	1.15	4.4	[e]	250
P_{II} **2**	[f]	0.78	2.6	[e]	250
P_{II} **3**	10.6 (37.3)	0.94	3.9	[e]	250
P_{II} **4**	10 (49)	0.65	5.6	[e]	240

[a] Weight (and maximum weight) percent of NLO dye in copolymer measured from ^{1}H-NMR.
[b] Apparent molecular weights measured by GPC in THF, polystyrene standards.
[c] Polydispersity: $D = \overline{M}_w/\overline{M}_n$.
[d] Decomposition temperature.
[e] T_g not detectable.
[f] Low solubility of the functionalised polymer.

Table 4
Wavelength of maximum absorption (λ_{max}) and second-harmonic coefficients of chromophore-functionalised poly(phenylmaleimide-urethane)s

Polymer	λ_{max} (nm)[a]	d_{33} (ω) (pm/V)[b]	$d_{33}(0)$ (pm/V)[c]
P_I **3**	474	7.6	1.25
P_I **4**	436	1	0.27
P'_I **1**	498	7.6	0.51
P'_I **3**	468	14.4	2.62
P'_I **4**	434	1	0.27
P_{II} **1**	503	2	0.16
P_{II} **3**	474	2.8	0.49
P_{II} **4**	436	0.36	0.09

[a] Measured in spin-coated 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) [35].

be corrected for absorption. Using the two level model, $d_{33}(0)$ values were calculated.

Dörr et al. [30] also studied poly(maleimide-urethane)s and found much higher d_{33} values compared to our results. Several possible reasons could be taken into account for our 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 lower poling efficiency. In addition, the materials used consist of chromophores with only moderate hyperpolarisabilities, which may also partially explain the low d_{33} values. Restricted mobility of the chromophores could be another reason. However our systems are side-chain polymers with a very typical and expected relaxation behaviour.

The stability of the NLO effect of P_I **3** and P'_I **3** was measured at 125°C. From the normalised second-harmonic coefficients as a function of time, where $d_{33}(t)/d_{33}(0)$ represents the second-harmonic coefficient at time t and time 0 respectively; it can be seen that after an initial decrease (30 h), the nonlinearity does not significantly change over 500 h, which finally results in 58% respectively 85% of remaining NLO efficiency.

4. Conclusion

We synthesised new chromophore-functionalised poly(N-phenylmaleimide)- and poly(N-biphenylmaleimide)-urethane copolymers, with high glass transition temperatures. This results in a stable NLO response at elevated temperatures. One of the polymer systems lost only 15% of its nonlinearity effect after 500 h of heating at 125°C. In addition, the magnitude of the NLO response suggests that these polymers could be useful for NLO applications.

Acknowledgements

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